

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 213 336 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
12.06.2002 Bulletin 2002/24

(51) Int Cl.7: **C09K 11/06**(21) Application number: **01310199.3**(22) Date of filing: **05.12.2001**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **06.12.2000 JP 2000371180**
30.03.2001 JP 2001100626

(71) Applicant: **Sumitomo Chemical Company,
Limited**
Chuo-ku Osaka 541-8550 (JP)

(72) Inventors:

• **Doi, Shuji**
Tsukuba-shi, Ibaraki (JP)

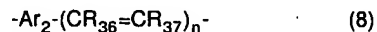
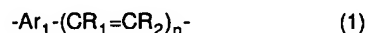
• **Tsubata, Yoshiaki**
Tsukuba-shi, Ibaraki (JP)
• **Ueoka, Takahiro**
Tsukuba-shi, Ibaraki (JP)
• **Sasaki, Shigeru**
Tsukuba-shi, Ibaraki (JP)
• **Noguchi, Takanobu**
Tsukuba-shi, Ibaraki (JP)

(74) Representative: **Cresswell, Thomas Anthony**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5JJ (GB)

(54) **Polymeric fluorescent substance and polymer light-emitting device using the same**

(57) A polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 1×10^3 to 1×10^8 , and comprising one or more repeating units of formula (1) and one or more repeating units of formula (8):

wherein Ar_1 represents a specific arylene or a divalent heterocyclic compound group, and Ar_2 represent an arylene or a divalent heterocyclic compound group other than Ar_1 . By using the polymeric fluorescent substance, a high performance polymer LED can easily be obtained.

**EP 1 213 336 A2**

Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a polymeric fluorescent substance and more specifically a polymer light-emitting device using the same.

10 Description of the Related Art

[0002] Differing from low molecular weight materials, light emitting materials having higher molecular weight (polymeric fluorescent substances) have a merit that they can be dissolved in a solvent, and can form a light emitting layer by a coating method, and various substances have been studied. For example, J. Mater. Sci. Mater. Ele., 11, p.111 (2000) describes polymers containing unsubstituted naphthalene and fluorene.

[0003] An object of the present invention is to provide: a polymeric fluorescent substance comprising a condensed aromatic ring such as naphthalene and an arylene group such as fluorene, and manifesting strong fluorescence; and a polymer LED of high performance which can be driven at lower voltage with high efficiency, using this polymeric fluorescent substance.

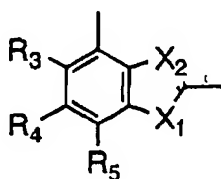
20 SUMMARY OF THE INVENTION

[0004] The present inventors have intensively studied in view of the above problems, and resultantly found that a polymeric fluorescent substance comprising a specific condensed aromatic ring having a substituent and an arylene group such as fluorene shows strong fluorescence, and a polymer LED of high performance which can be driven at lower voltage with high efficiency can be obtained using the above-mentioned polymeric fluorescent substance, leading to completion of the invention.

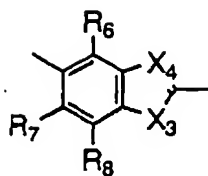
[0005] Namely, the present invention relates to a polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 1×10^3 to 1×10^8 , and comprising one or more repeating units of the following general formula (1) and one or more repeating units of formula (8),



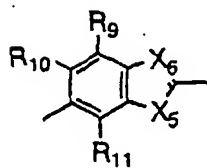
35 In the formula, Ar_1 is a divalent group represented by the following formulae (2) to (7); R_1 and R_2 each independently represent a group selected from a hydrogen atom, alkyl groups, aryl groups, monovalent heterocyclic compound groups and cyano group; and n is 0 or 1,



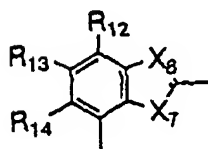
(2)



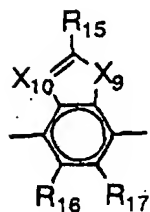
(3)



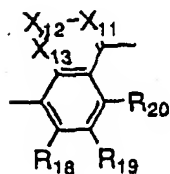
(4)



(5)



(6)



(7)

[0006] In formulae (2) to (7), X_1 , X_3 , X_5 , X_7 and X_9 each independently represent a group selected from $-CR_{21}=CR_{22}-$, $-CR_{23}=N-$, $-N=CR_{24}-$, $-O-CO-$, $-CR_{25}R_{26}-$, $-CO-$, $-O-$, $-S-$, $-Se-$, $-NR_{27}-$ and $-SiR_{28}R_{29}-$; X_2 , X_4 , X_6 , X_8 and X_{10} each independently represent a group selected from $-CR_{30}=$ and $-N=$; R_3 to R_{30} each independently represent a hydrogen atom or a substituent selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylaminogroup, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylami-

no group, arylalkenyl group, arylalkinyl group, monovalent heterocyclic compound group and cyano group; at least one of R_3 to R_{30} is not a hydrogen atom.



In the formula, Ar_2 represents an arylene group or divalent heterocyclic compound group, but the group is not represented by any of formulae (2) to (7); Ar_2 may have one or more substituents; when Ar_2 has a plurality of substituents, they may be the same or different; R_{36} and R_{37} each independently represent a group selected from a hydrogen atom, alkyl groups, aryl groups, monovalent heterocyclic compound groups and a cyano group; and n represents 0 or 1.

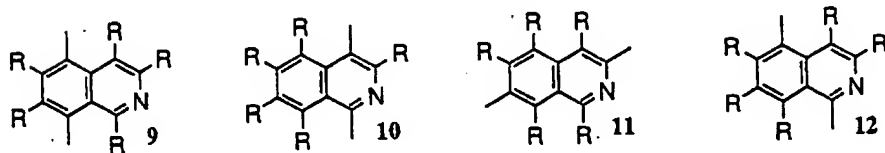
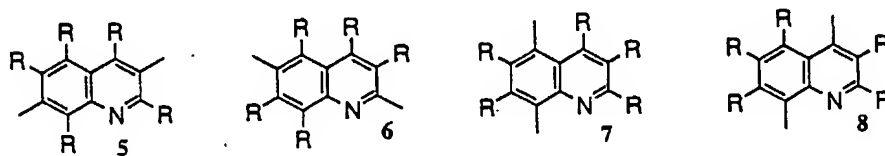
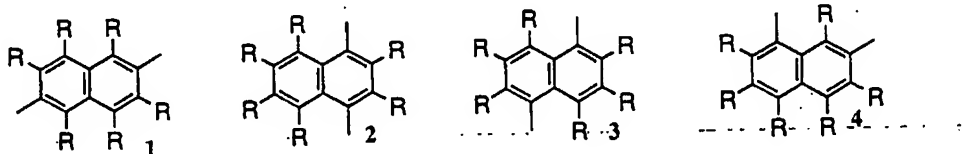
Also, the present invention relates to a polymer light emitting device comprising at least a light emitting layer between a pair of electrodes composed of an anode and a cathode at least one of which is transparent or semi-transparent wherein the light emitting layer comprises the above polymeric fluorescent substance.

[0007] Further, the present invention relates to a flat light source, a segment display, and a dot matrix display, obtained by using the above polymer light emitting device. Furthermore, the present invention relates to a liquid crystal display obtained by using the above polymer light emitting device as a back-light.

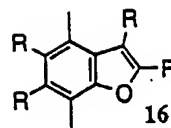
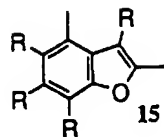
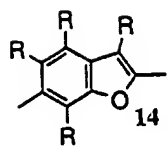
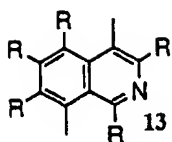
DETAILED DESCRIPTION OF THE INVENTION

[0008] In the polymeric fluorescent substance of the present invention, Ar_1 has one or more substituents which are not hydrogen atom.

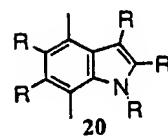
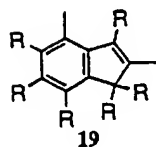
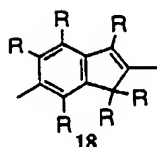
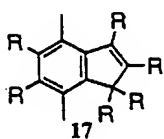
[0009] Examples of Ar_1 include: the following structures of Nos. 4, 15, 19, 22, 25, 28, 31, and 35, as a divalent group shown by formula (2); following structures of Nos. 39, 40, 41, 42, and 43, as a divalent group shown by formula (3); following structures of Nos. 1, 5, 6, 11, 14, 18, 21, 24, 27, 30, 34, 36, and 37, as a divalent group shown by formula (4); following structures of Nos. 44, 45, 46, 47, and 48, as a divalent group shown by formula (5); following structures of Nos. 2, 7, 9, 16, 17, 20, 23, 26, 29, 32, 33, and 38, as a divalent group shown by formula (6); and following structures of Nos. 3, 12, and 13, as a divalent group shown by formula (7). In the structures, at least one of the R s is not a hydrogen atom. Among them, the structures represented by formula (4) are preferable.



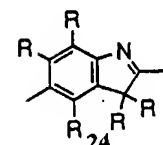
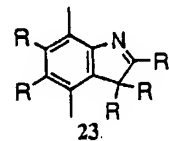
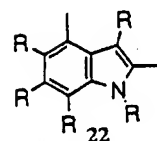
5



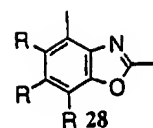
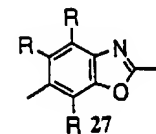
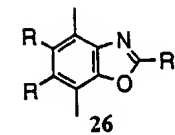
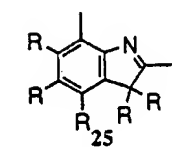
10



15

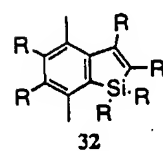
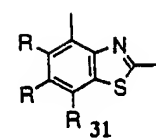


20



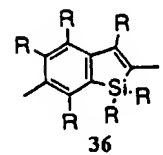
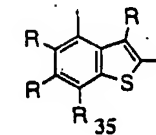
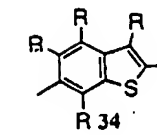
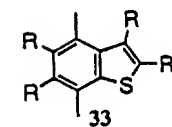
25

30



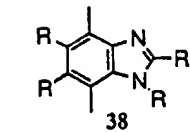
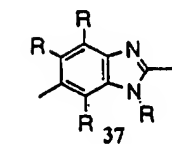
35

40

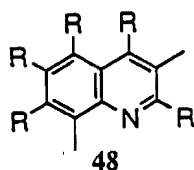
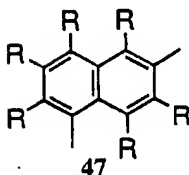
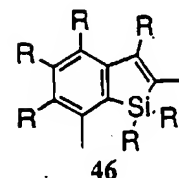
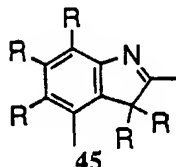
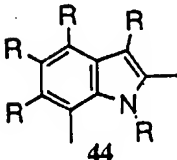
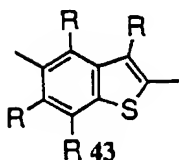
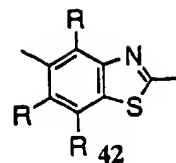
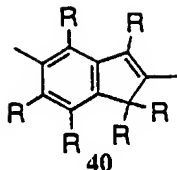
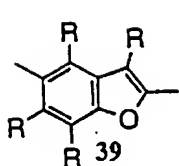


45

50



55



[0010] Here, R (namely, R_3 to R_{30}) represents each independently a group selected from a hydrogen atom, alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, aryl alkylamino group, arylalkenyl group, and aryl alkynyl group.

[0011] In order to improve the solubility in a solvent, it is suitable to have one or more substituents, and it is preferable that the repeating unit including substituent has a form of little symmetry.

[0012] The alkyl group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof include specifically methyl group, ethyl group, propyl group, i-propyl group, butyl group, i-butyl group, t-butyl group, pentyl group, hexyl group, cyclohexyl group, heptyl group, octyl group, 2-ethylhexyl group, nonyl group, decyl group, 3,7-dimethyloctyl group, lauryl group, etc. Among them, pentyl group, hexyl group, octyl group, 2-ethylhexyl group, decyl group, and 3,7-dimethyl octyl group are preferable.

[0013] The alkoxy group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof include specifically methoxy group, ethoxy group, propoxy group, i-propoxy group, butoxy group, i-butoxy group, t-butoxy group, pentyloxy group, hexyloxy group, cyclohexyloxy group, heptyloxy group, octyloxy group, 2-ethylhexyloxy group, nonyloxy group, decyloxy group, 3,7-dimethyloctyloxy group, lauryloxy group etc. Among them, pentyloxy group, hexyloxy group, octyloxy group, 2-ethylhexyloxy group, decyloxy group, and 3,7-dimethyl octyloxy group are preferable.

[0014] The alkylthio group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof include specifically methylthio group, ethylthio group, propylthio group, and i-propylthio group, butylthio group, i-butylthio group, t-butylthio group, pentylthio group, hexylthio group, cyclohexylthio group, heptylthio group, octylthio group, 2-ethylhexylthio group, nonylthio group, decylthio group, 3,7-dimethyloctylthio group, laurylthio group etc. Among them, pentylthio group, hexylthio group, octylthio group, 2-ethylhexylthio group, decylthio group, and 3,7-dimethyloctylthio group are preferable.

[0015] The alkylsilyl group may be linear, branching or cyclic, and has usually about one to 60 carbon atoms. Examples thereof include specifically methylsilyl group, ethylsilyl group, propylsilyl group, and i-propylsilyl group, butylsilyl group, i-butylsilyl group, t-butylsilyl group, pentylsilyl group, hexylsilyl group, cyclohexylsilyl group, heptylsilyl group, octylsilyl group, 2-ethylhexylsilyl group, nonylsilyl group, decylsilyl group, 3,7-dimethyloctylsilyl group, laurylsilyl group, trimethylsilyl group, ethyldimethylsilyl group, propyldimethylsilyl group, i-propyldimethylsilyl group, butyldimethylsilyl group, t-butyldimethylsilyl group, pentyldimethylsilyl group, hexyldimethylsilyl group, heptyldimethylsilyl group, octyldimethylsilyl group, 2-ethylhexyldimethylsilyl group, nonyldimethylsilyl group, decyldimethylsilyl group, 3,7-dimethyloc-

tyl-dimethylsilyl group, lauryldimethylsilyl group, etc. Among them, pentylsilyl group, hexylsilyl group, octylsilyl group, 2-ethylhexylsilyl group, decylsilyl group, 3,7-dimethyloctylsilyl group, pentyldimethylsilyl group, hexyldimethylsilyl group, octyldimethylsilyl group, 2-ethylhexyl-dimethylsilyl group, decyldimethylsilyl group, 3,7-dimethyloctyl-dimethylsilyl group are preferable.

[0016] The alkylamino group may be linear, branching or cyclic, and has usually about one to 40 carbon atoms. Either monoalkylamino group or dialkylamino group may be available. Examples thereof include specifically methylamino group, dimethylamino group, ethylamino group, diethylamino group, propylamino group, i-propylamino group, butylamino group, i-butylamino group, t-butylamino group, pentylamino group, hexylamino group, cyclohexylamino group, heptylamino group, octylamino group, 2-ethylhexylamino group, nonylamino group, decylamino group, 3,7-dimethyloctylamino group, laurylamino group, etc. Among them, pentylamino group, hexylamino group, octylamino group, 2-ethylhexylamino group, decylamino group, and 3,7-dimethyloctylamino group are preferable.

[0017] The aryl group has usually about 6 to 60 carbon atoms. Examples thereof include phenyl group, C₁₋₁₂ alkoxyphenyl group (C₁₋₁₂ means that the number of carbon atoms is from 1 to 12), C₁₋₁₂ alkylphenyl group, 1-naphthyl group, 2-naphthyl group, etc. Among them, C₁₋₁₂ alkoxyphenyl group, and C₁₋₁₂ alkylphenyl group are preferable.

[0018] The aryloxy group has usually about 6 to 60 carbon atoms. Examples thereof include specifically, phenoxy group, C₁₋₁₂ alkoxyphenoxy group, C₁₋₁₂ alkylphenoxy group, 1-naphtyloxy group, 2-naphtyloxy group, etc. Among them, C₁₋₁₂ alkoxyphenoxy group, and C₁₋₁₂ alkylphenoxy group are preferable.

[0019] The arylsilyl group has usually about 6 to 60 carbon atoms. Examples thereof include specifically, phenylsilyl group, C₁₋₁₂ alkoxyphenylsilyl group, C₁₋₁₂ alkylphenylsilyl group, 1-naphtylsilyl group, 2-naphtylsilyl group, dimethylphenylsilyl group, etc. Among them, C₁₋₁₂ alkoxyphenylsilyl group and C₁₋₁₂ alkylphenylsilyl group are preferable.

[0020] The arylamino group has usually about 6 to 60 carbon atoms. Examples thereof include specifically, diphenylamino group, C₁₋₁₂ alkoxyphenylamino group, di(C₁₋₁₂ alkoxyphenyl)amino group, di(C₁₋₁₂ alkylphenyl)amino group, 1-naphtylamino group, 2-naphtylamino group, etc. Among them C₁₋₁₂ alkylphenylamino group, and di(C₁₋₁₂ alkylphenyl)amino group are preferable.

[0021] The arylalkyl group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkyl group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkyl group, C₁₋₁₂ alkylphenyl-C₁₋₁₂alkyl group, 1-naphtyl-C₁₋₁₂alkyl group, 2-naphtyl-C₁₋₁₂alkyl group, etc. Among them, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkyl group, and C₁₋₁₂alkylphenyl-C₁₋₁₂alkyl group are preferable.

[0022] The arylalkoxy group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkoxy group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkoxy group, C₁₋₁₂alkylphenyl-C₁₋₁₂alkoxy group, 1-naphtyl-C₁₋₁₂alkoxy group, 2-naphtyl-C₁₋₁₂alkoxy group, etc. Among them, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkoxy group, and C₁₋₁₂alkylphenyl-C₁₋₁₂alkoxy group are preferable.

[0023] The arylalkylsilyl group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkylsilyl group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkylsilyl group, C₁₋₁₂alkylphenyl-C₁₋₁₂alkylsilyl group, 1-naphtyl-C₁₋₁₂alkylsilyl group, 2-naphtyl-C₁₋₁₂alkylsilyl group, phenyl-C₁₋₁₂alkyldimethylsilyl group, etc. Among them, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkylsilyl group, and C₁₋₁₂alkylphenyl-C₁₋₁₂alkylsilyl group are preferable.

[0024] The arylalkylamino group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkylamino group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkylamino group, C₁₋₁₂alkylphenyl-C₁₋₁₂alkylamino group, di(C₁₋₁₂ alkoxyphenyl-C₁₋₁₂alkyl)amino group, di(C₁₋₁₂ alkylphenyl-C₁₋₁₂alkyl)amino group, 1-naphtyl-C₁₋₁₂alkylamino group, 2-naphtyl-C₁₋₁₂alkylamino group, etc. Among them, C₁₋₁₂alkylphenyl-C₁₋₁₂alkylamino group, and di(C₁₋₁₂ alkylphenyl-C₁₋₁₂alkyl)amino group are preferable.

[0025] The arylalkenyl group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkenyl group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkenyl group, C₁₋₁₂alkylphenyl-C₁₋₁₂alkenyl group, 1-naphtyl-C₁₋₁₂alkenyl group, 2-naphtyl-C₁₋₁₂alkenyl group, etc. Among them, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkenyl group, and C₁₋₁₂alkylphenyl-C₁₋₁₂alkenyl group are preferable.

[0026] The arylalkynyl group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkynyl group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkynyl group, C₁₋₁₂alkylphenyl-C₁₋₁₂alkynyl group, 1-naphtyl-C₁₋₁₂alkynyl group, 2-naphtyl-C₁₋₁₂alkynyl group, etc. Among them, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkynyl group, and C₁₋₁₂alkylphenyl-C₁₋₁₂alkynyl group are preferable.

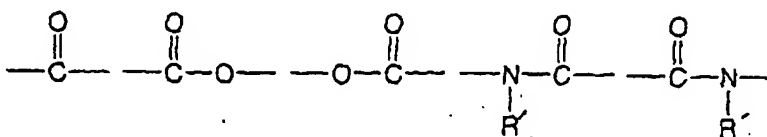
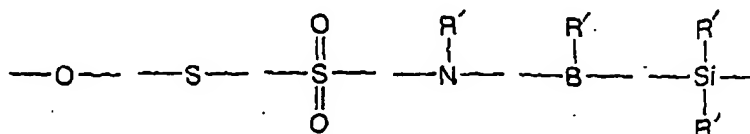
[0027] The monovalent heterocyclic compound group means an atomic group of a heterocyclic compound in which one hydrogen atom is removed, and has usually about 4 to 60 carbon atoms. Examples thereof include thienyl group, C₁₋₁₂alkylthienyl group, pyroryl group, furyl group, pyridyl group, C₁₋₁₂alkylpyridyl group, etc. Among them, thienyl group, C₁₋₁₂alkylthienyl group, pyridyl group, and C₁₋₁₂alkylpyridyl group are preferable.

[0028] In the substituents containing an alkyl chain among the examples of R, said alkyl chain may be linear, branching or cyclic. Combination thereof may be also included. When the alkyl chain is not linear, examples thereof include iso-amyl group, 2-ethylhexyl group, 3,7-dimethyloctyl group, cyclohexyl group, 4-C₁₋₁₂alkylcyclohexyl group, etc.

[0029] In order to improve the solubility of a polymeric fluorescent substance in a solvent, it is suitable that at least one substituent of Ar₁ contains an alkyl chain having cyclic or branching structure. Moreover, the alkyl chain may be

interrupted with a group containing a hetero atom, $-\text{CR}_{31}=\text{CR}_{32}-$, or $-\text{C}\equiv\text{C}-$.

[0030] Here, as a hetero atom, an oxygen atom, a sulfur atom, a nitrogen atom, etc. are exemplified. Examples of the group containing a hetero atom include the following groups.



[0031] R' means, for example, hydrogen atom, alkyl group having 1 to 20 carbon atoms, aryl group having 6 to 60 carbon atoms, and monovalent heterocyclic compound group having 4 to 60 carbon atoms. R₃₁ and R₃₂ mean the same with the examples of R₁ and R₂ below recited.

[0032] Furthermore, when an aryl group or a monovalent heterocyclic compound group is included in R as a part of the structure, the group may have one more or more substituents.

Moreover, one or more hydrogen atoms contained in the repeating unit represented by formula (1) may be substituted by a halogen atom selected from F, Cl and Br.

[0033] In formula (1), n is 0 or 1. R₁ and R₂ in formula (1) represent each independently a group selected from a hydrogen atom, an alkyl group, an aryl group, a monovalent heterocyclic compound group, and a cyano group.

[0034] In the case where R₁ and R₂ are substituents other than a hydrogen atom or a cyano group, the alkyl group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof include specifically methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, lauryl group, etc. Among them, methyl group, ethyl group, pentyl group, hexyl group, heptyl group, and an octyl group are preferable.

[0035] The aryl group has usually about 6 to 60 carbon atoms. Examples thereof include specifically phenyl group, C₁₋₁₂ alkoxyphenyl group, C₁₋₁₂ alkylphenyl group, 1-naphtyl group, 2-naphtyl group, etc. Among them, phenyl group and C₁₋₁₂ alkylphenyl group are preferable.

[0036] The monovalent heterocyclic compound group has usually about 4 to 60 carbon atoms. Examples thereof include specifically thienyl group, C₁₋₁₂ alkylthienyl group, pyroryl group, furyl group, pyridyl group, C₁₋₁₂ alkylpyridyl group, etc. Among them, thienyl group, C₁₋₁₂ alkylthienyl group, pyridyl group, and C₁₋₁₂ alkylpyridyl group are preferable.

[0037] The polymeric fluorescent substance of the present invention has the repeating unit represented by the following formula (8) as a repeating unit other than formula (1).



[0038] Here, Ar₂ represents an arylene group or a divalent heterocyclic compound group, and R₃₆ and R₃₇ show each independently a group selected from a hydrogen atom, an alkyl group, an aryl group, a monovalent heterocyclic compound group, and a cyano group. The symbol m is 0 or 1.

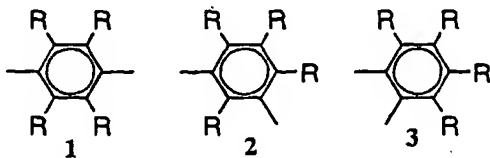
[0039] In formula (8), Ar₂ is an arylene group or a divalent heterocyclic compound group, and is not a group shown by any one of formulae (2) to (7). Ar₂ may have one or more substituents. When Ar₂ has a plurality substituents, they may be the same or different.

[0040] The arylene group includes those having a benzene ring, a condensed ring, and those in which independent benzene rings and/or condensed rings are bonded directly or through groups such as vinylene. The arylene group has usually 6 to 60 carbon atoms, preferably 6 to 20. Examples thereof include: phenylene groups (for example, the below structures of Nos. 1 to 3), naphthalenediyl groups (the below structures of Nos. 4 to 13), anthracenylenes groups (the

below structures of Nos. 14 to 19), biphenylene groups (the below structures of Nos. 20 to 25), triphenylene groups (the below structures of Nos. 26 to 28), stilbene-diyl (the below structures of A to D), distilbene-diyl (the below structures of E and F), condensed-ring compound groups (the below structures of Nos. 29 to 38), etc. Here, the number of carbon atoms of the substituent is not counted as the number of carbon atoms of the arylene group.

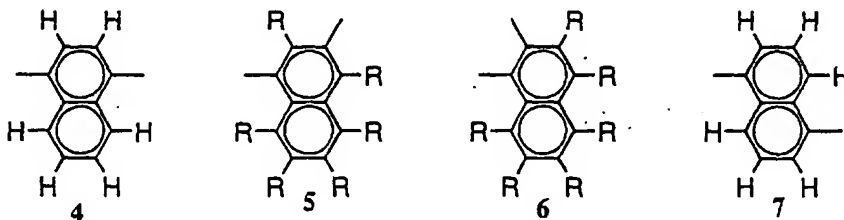
5

10



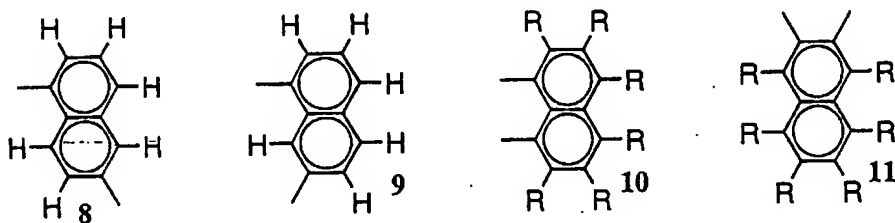
15

20



25

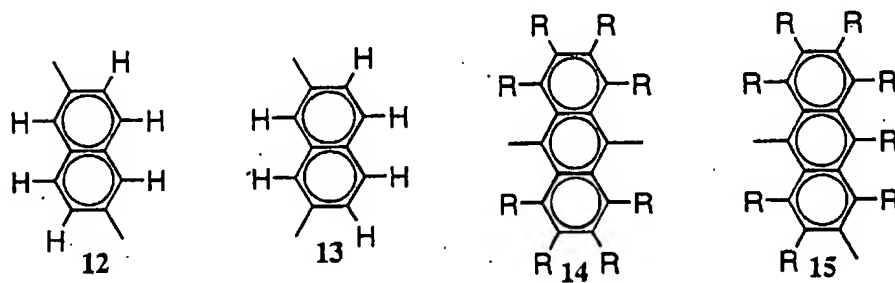
30



35

40

45



50

55

5

10

15

20

25

30

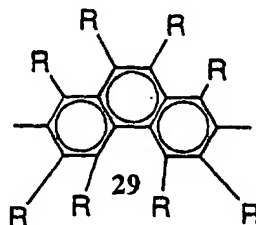
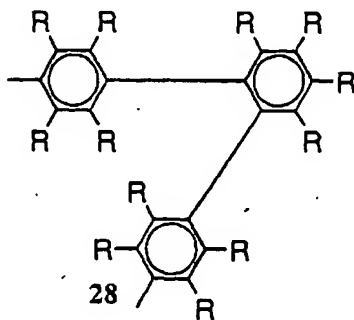
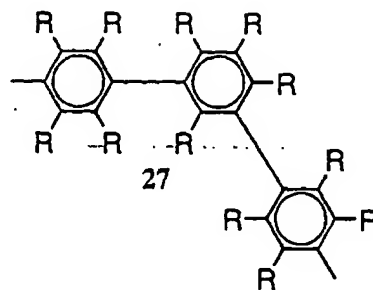
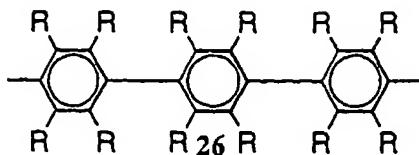
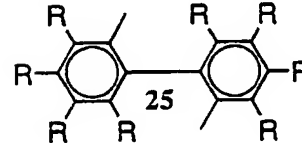
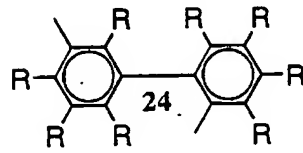
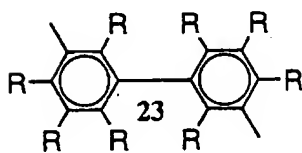
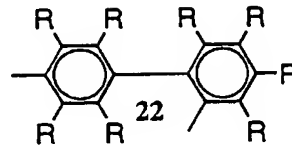
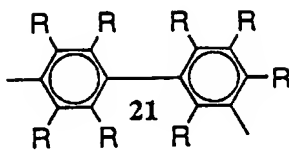
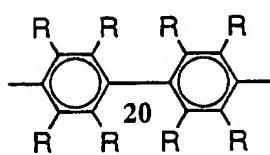
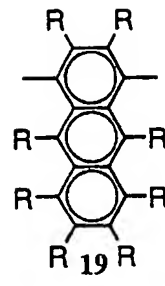
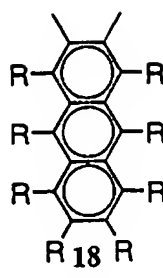
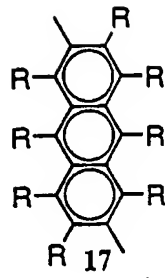
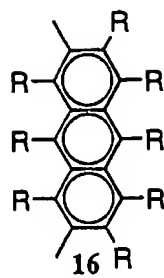
35

40

45

50

55



5

10

15

20

25

30

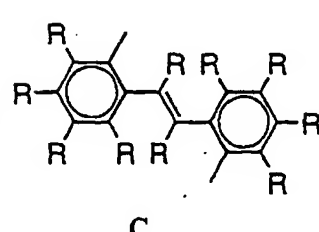
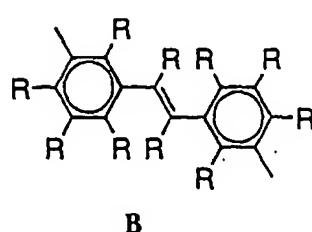
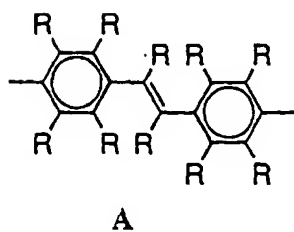
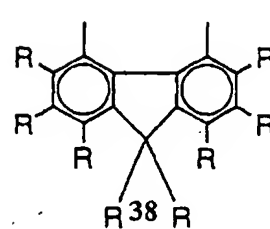
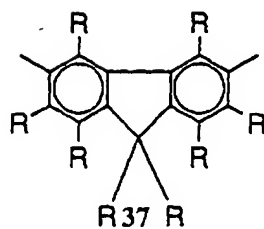
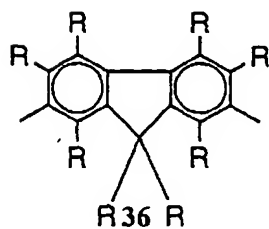
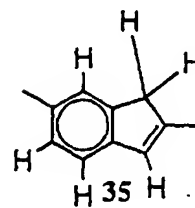
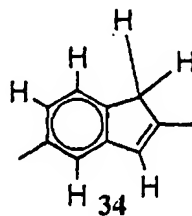
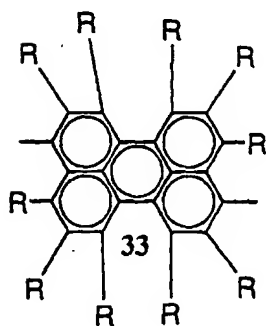
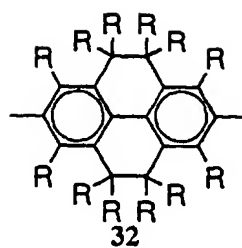
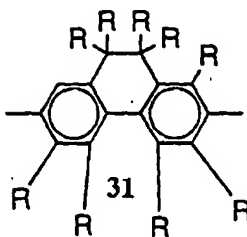
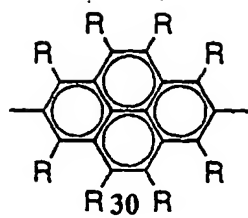
35

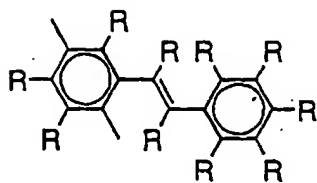
40

45

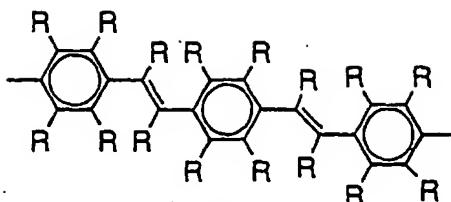
50

55

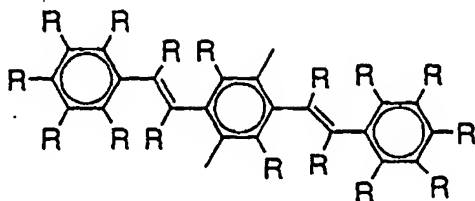




D



E



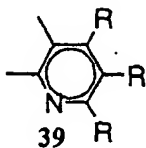
F

[0041] The divalent heterocyclic compound group means an atomic group of a heterocyclic compound in which two hydrogen atoms are removed, and has usually about 4 to 60, preferably 4 to 20 carbon atoms. Here, the number of carbon atoms of the substituent is not counted as the number of carbon atoms of the divalent heterocyclic compound group.

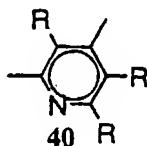
[0042] Here, the heterocyclic compound means that an organic compound having a cyclic structure in which at least one heteroatom such as oxygen, sulfur, nitrogen, phosphor, boron, etc. is contained in the cyclic structure as the element other than carbon atoms.

Examples of the divalent heterocyclic compound group include: divalent heterocyclic compound groups containing nitrogen as the heteroatom, such as: pyridine-diyl groups (the below structures of Nos. 39 to 44), diazaphenylene groups (the below structures of Nos. 45 to 48), quinoxalinediyl groups (the below structures of Nos. 49 to 63), quinoxalinediyl groups (the below structures of Nos. 64 to 68), acridinediyl groups (the below structures of Nos. 69 to 72), bipyridyldiyl groups (the below structures of Nos. 73 to 75), phenanthrolinediyl groups (the below structures of Nos. 76 to 78), etc.; groups having fluorene structure containing silicon, nitrogen, sulfur, selenium, etc. as the hetero atom (the below structures of Nos. 79 to 93); 5-membered-ring heterocyclic compound groups containing silicon, nitrogen, sulfur, selenium, etc. as the heteroatom (the below structures of Nos. 94 to 98); 5-membered-ring condensed heterocyclic compound groups containing silicon, nitrogen, sulfur, selenium, etc. as the heteroatom (the below structures of Nos. 99 to 110); groups of 5-membered-ring heterocyclic compound groups containing silicon, nitrogen, sulfur, selenium, etc. as the heteroatom, which form dimer or oligomer by bonding at α -position of the hetero atom (the below structures of Nos. 111 to 112); and

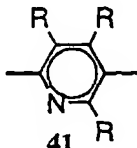
groups of 5-membered-ring heterocyclic compound groups containing silicon, nitrogen, sulfur, selenium, etc. as the heteroatom, which bond to a phenyl group at α -position of the hetero atom (the below structures of Nos. 113-119).



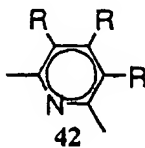
39



40



41

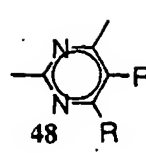
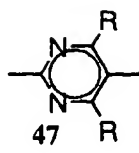
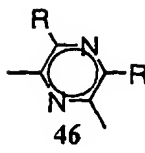
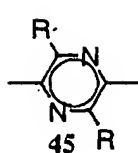
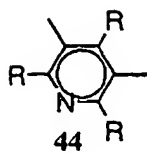


42

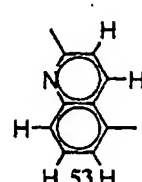
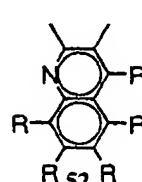
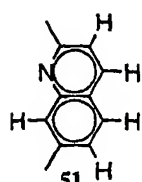
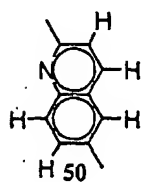
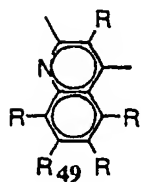


43

5

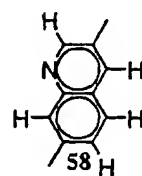
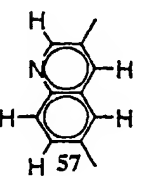
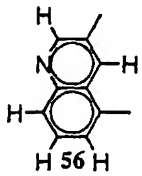
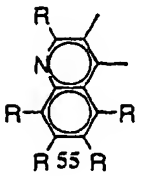
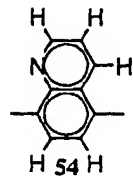


10



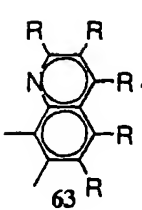
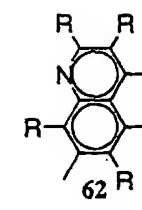
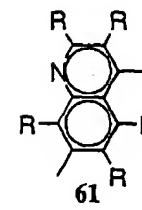
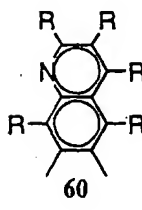
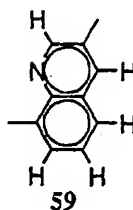
15

20



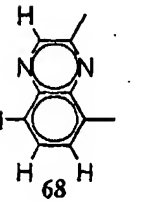
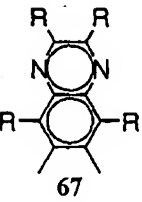
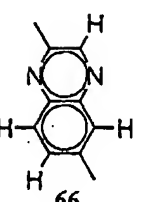
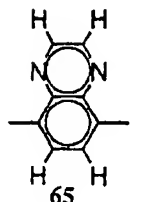
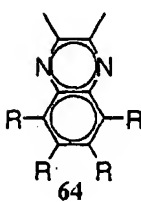
25

30



35

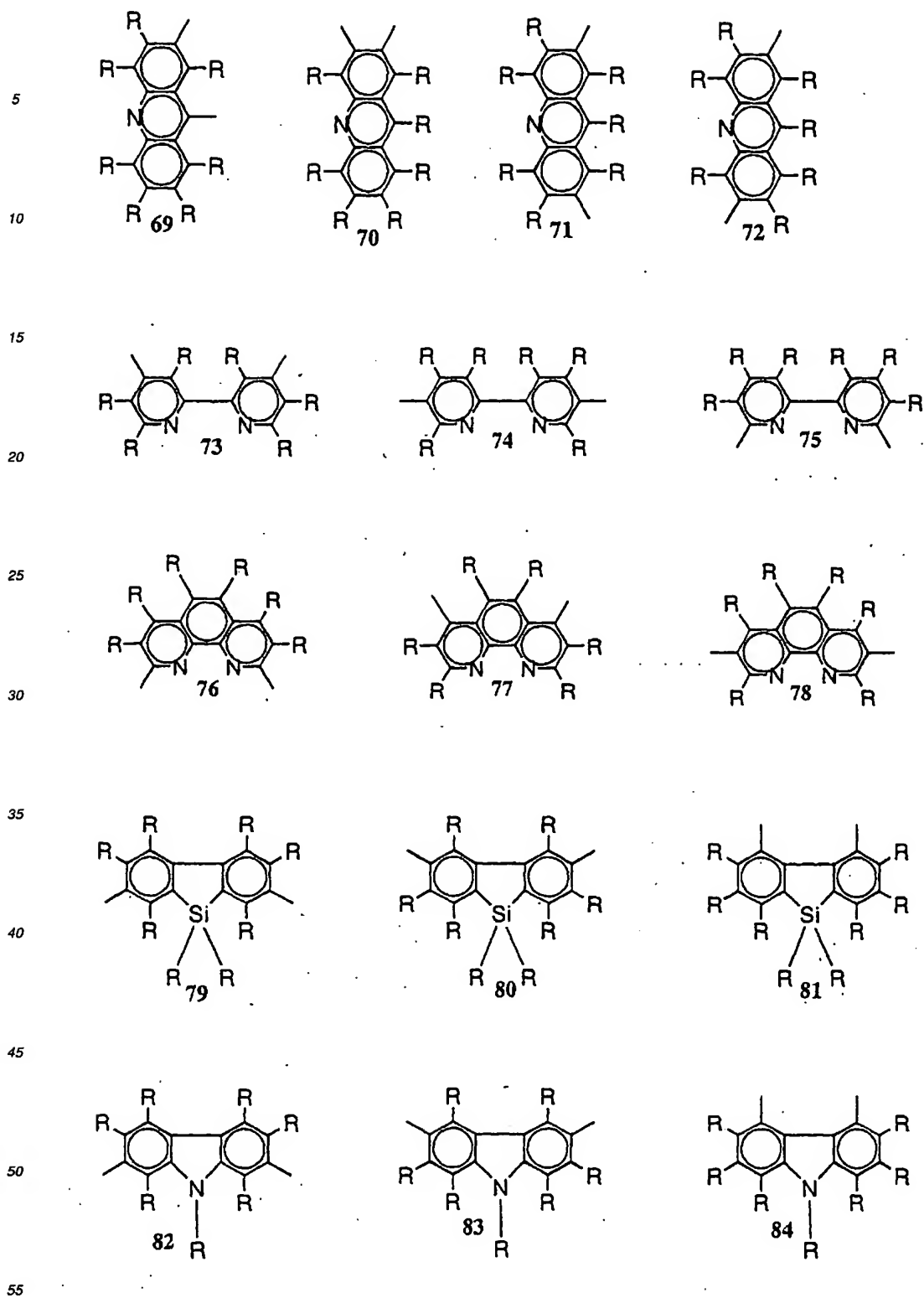
40

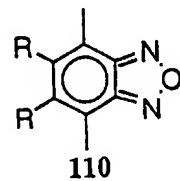
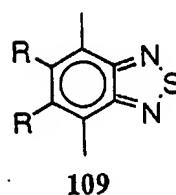
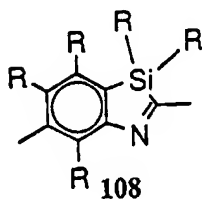
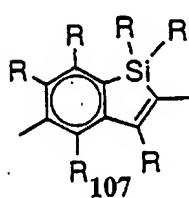
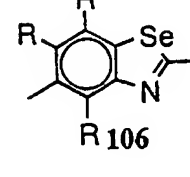
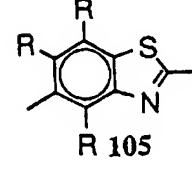
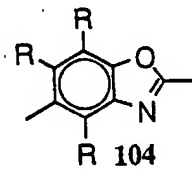
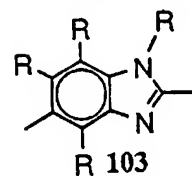
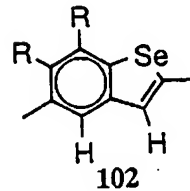
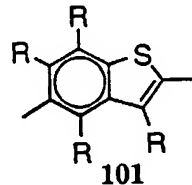
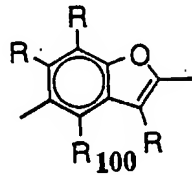
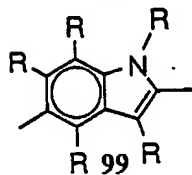
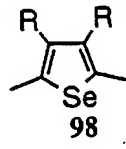
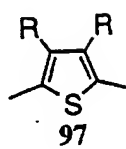
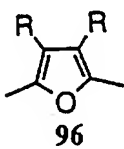
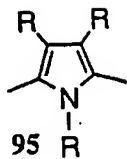
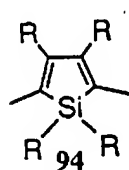
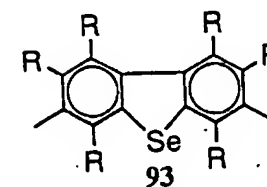
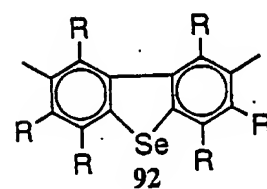
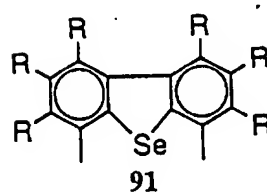
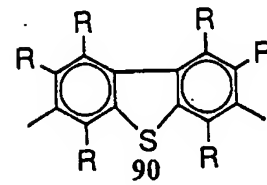
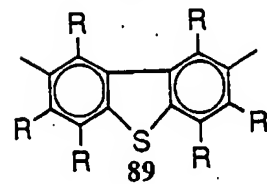
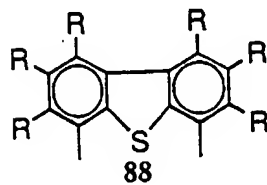
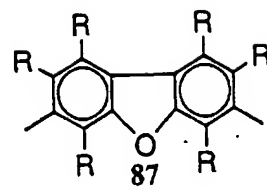
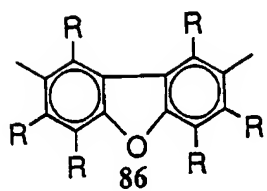
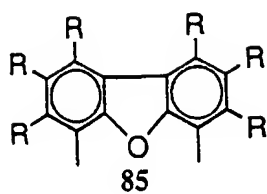


45

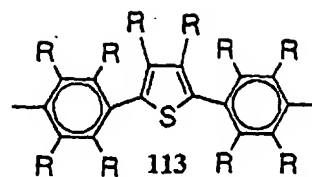
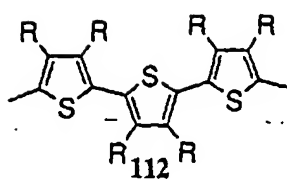
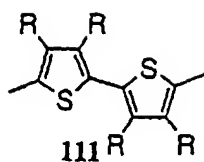
50

55

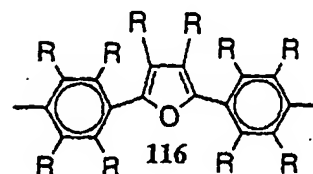
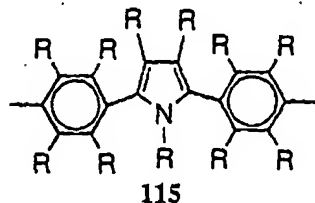
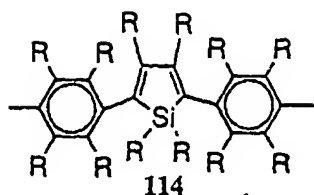




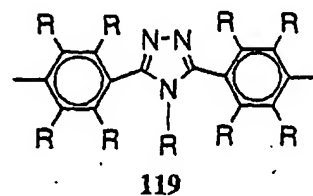
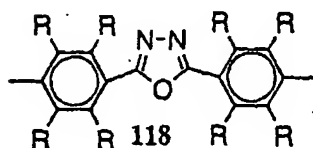
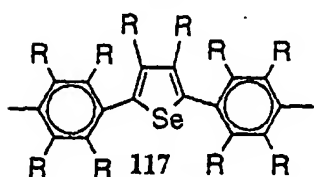
5



10



15



20

25

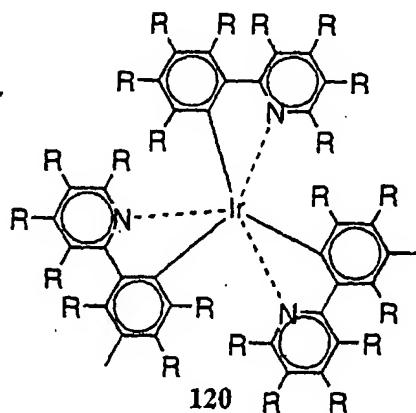
[0043] Furthermore, as a divalent heterocyclic compound group, for example, a complex emitting triplet luminescence, etc. are included. Examples thereof include divalent metal complex groups shown below (Nos. 120 to 126).

30

35

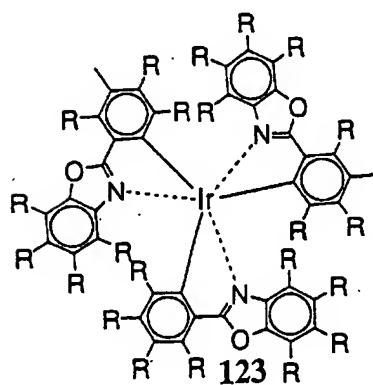
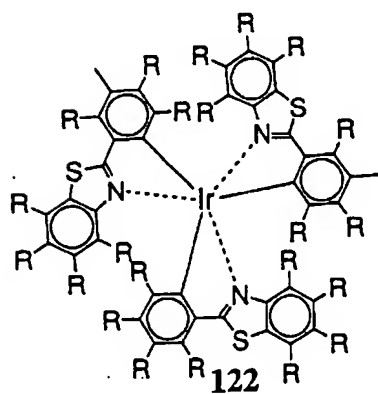
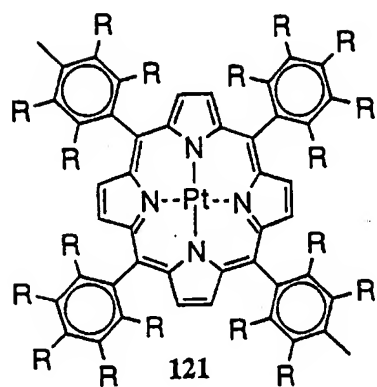
40

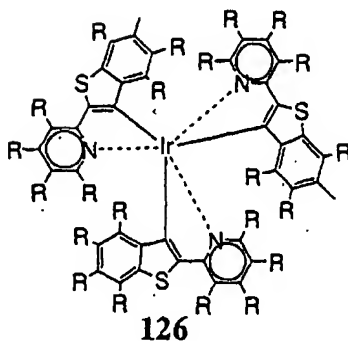
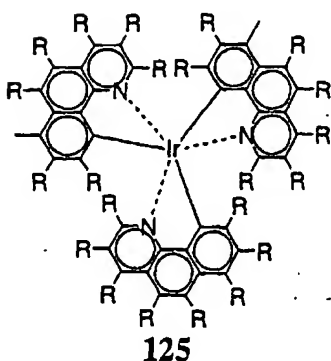
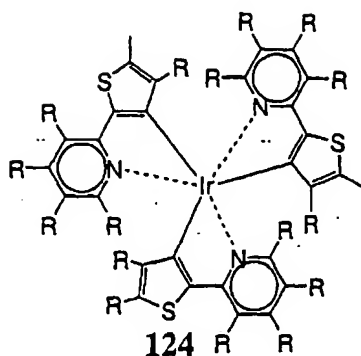
45



50

55





[0044] Here, R means the same with the R of the divalent groups described above as the examples of Ar₁. Examples and preferable examples thereof also include the same with those of Ar₁.

[0045] In formula (8), m is 0 or 1. R₃₆ and R₃₇ in formula (8) show each independently a group selected from a hydrogen atom, an alkyl group, an aryl group, a monovalent heterocyclic compound group, and cyano group.

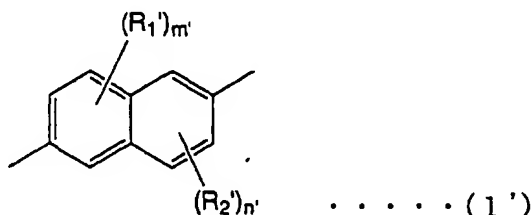
[0046] Examples and preferable examples of R₃₆ and R₃₇ are the same with those exemplified in the example of R₁ and R₂ described above.

[0047] The total amount of repeating units represented by the formulae (1) and (8) is usually 50 mol% or more based on the total amount of all repeating units, and preferably 70 mol% or more. And the amount of repeating unit represented by the formula (1) is usually 0.1 mol% or more and 95 mol% or less based on the total amount of the repeating units represented by the formulae (1) and (8), more preferably 5 mol% or more and 95 mol% or less, and further preferably

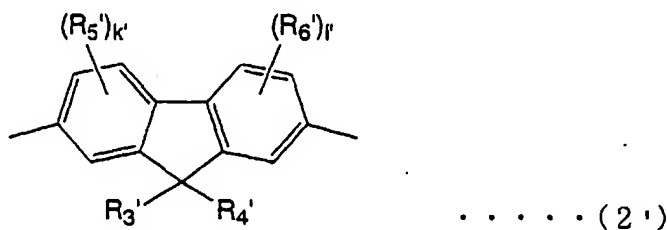
7 mol% or more and 80 mol% or less.

[0048] Furthermore, in order to obtain a polymeric fluorescent substance having excellent luminescence characteristics and solubility, it is suitable that Ar₁ of formula (1) has one or more groups as the substituents selected from an aryl group and a monovalent heterocyclic compound group.

Examples of the suitable combinations of formulae (1) and (8) for obtaining excellent polymeric fluorescent substances include: a polymeric fluorescent substance in which Ar₁ in formula (1) is represented by the below formula (1'); a polymeric fluorescent substance in which Ar₂ in formula (8) is represented by the below formula (2'); and a polymeric fluorescent substance in which Ar₁ in formula (1) is represented by formula (1') and Ar₂ in formula (8) is represented by formula (2').



In the formula, R₁' and R₂' represent each independently a group selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; m' and n' are integers of 0-3 each independently; However, m' and n' are not 0 simultaneously; when m' is two or more, two or more R₁' may be the same or different; when n' is two or more, plurality of R₂' may be the same or different; moreover, R₁' and R₂' may be connected to form a ring; furthermore, when R₁' and R₂' contain an alkyl chain, said alkyl chain may be interrupted by a group containing a hetero atom.



In the formula, R₃' and R₄' represent independently a group selected from a hydrogen atom, alkyl group, aryl group, and a heterocyclic compound group; R₅' and R₆' show each independently a group selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; k' and l' are integers of 0-3 each independently; when k' is two or more, plurality of R₅' may be the same or different; when l' is two or more, plurality of R₆' may be the same or different; R₃' - R₆' may be connected to form a ring; furthermore, in the case of the group in which R₃' - R₆' contains an alkyl chain, this alkyl chain may be interrupted by a group containing a hetero atom.

[0049] When Ar₁ is represented by formula (1') and Ar₂ is represented by formula (2'), it is preferable that the total amount of repeating units represented by the formulae (1) and (8) is 50 mol% or more based on the total amount of all repeating units. And the amount of repeating unit represented by the formula (1) is preferably 0.1 mol% or more and 50 mol% or less based on the total amount of the repeating units represented by the formulae (1) and (8).

[0050] Further, a protecting group may be used to stabilize the terminal group of a polymeric fluorescent substance in accordance with the present invention since if an active polymerizable group remains intact, there is a possibility of reduction of the light emitting property and life of the polymeric fluorescent substance when the material is used in a device.

[0051] Protecting groups having a conjugated bond continued to the conjugated structure of the main chain are preferable, and examples thereof include structures containing a bond to an aryl group or a heterocyclic compound group via a vinylene group. Specifically, protecting groups described in JP-A No. 9-45478, chemical formula 10, and

the like are exemplified.

[0052] This polymeric fluorescent substance may also be a random, block or graft copolymer, or a polymer having an intermediate structure thereof, for example, a random copolymer having blocking property. From the viewpoint for obtaining a polymeric fluorescent substance having high fluorescent quantum yield, random copolymers having blocking property and block or graft copolymers are more preferable than complete random copolymers. Further, copolymers may have a branched main chain and have three or more terminals. Dendrimers are also included.

[0053] Further, as the polymeric fluorescent substance, those emitting fluorescence in a solid state are suitably used, since the material utilizes light emission from a thin film.

[0054] As good solvents for the polymeric fluorescent substance, there are exemplified chloroform, methylene chloride, dichloroethane, tetrahydrofuran, toluene, xylene, mesitylene, tetralin, decalin, n-butylbenzene and the like. The polymeric fluorescent substance can be usually dissolved in these solvents in an amount of 0.1 wt % or more, though the amount differs depending on the structure and molecular weight of the polymeric fluorescent substance.

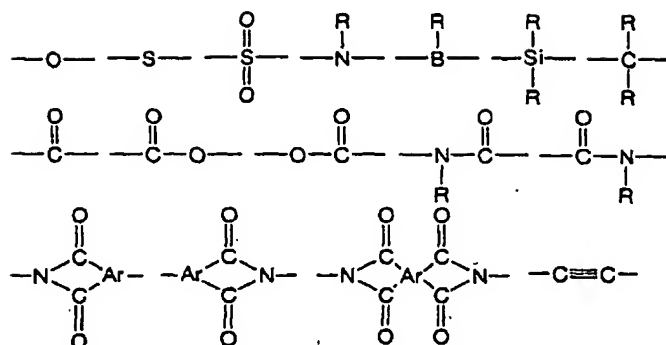
[0055] The polymeric fluorescent substance has a polystyrene-reduced number-average molecular weight of 10^3 to 10^8 , and the degree of polymerization thereof also changes depending on repeating structures and proportion thereof. From the standpoint of film forming property, generally the total amount of repeating structures is preferably from 20 to 10000, more preferably from 30 to 10000, particularly preferably from 50 to 5000.

[0056] When these polymeric fluorescent substances are used as a light emitting material of a polymer LED, the purity thereof exerts an influence on light emitting property, therefore, it is preferable that a monomer before polymerization is purified by a method such as distillation, sublimation purification, re-crystallization and the like before being polymerized and further, it is preferable to conduct a purification treatment such as re-precipitation purification, chromatographic separation and the like after the synthesis.

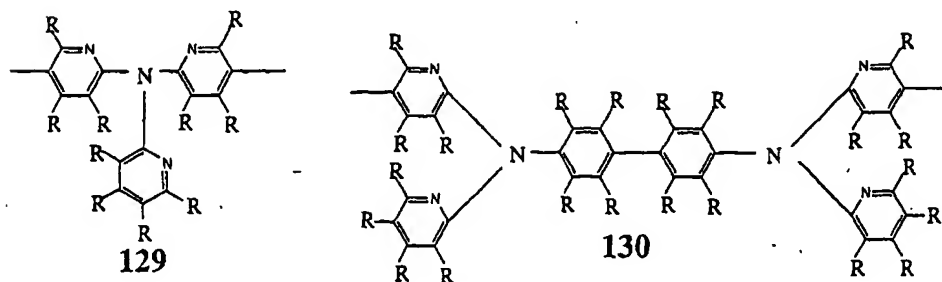
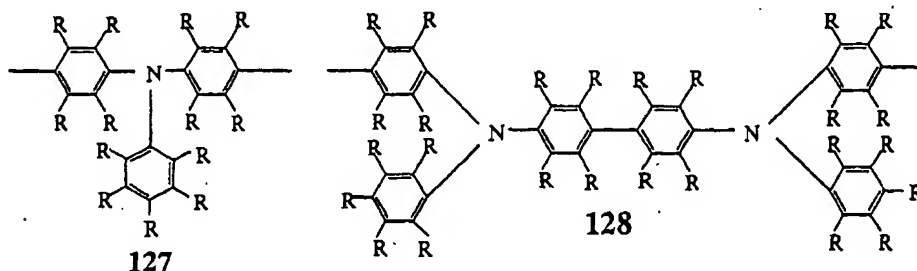
[0057] As methods described in JP-A No. 5-202355, may for example, be utilized when the main chain has a vinylene group. Namely, exemplified are: a polymerization of a dialdehyde compound with a diphosphonium salt compound according to the Wittig reaction; a polymerization of a divinyl compound with a dihalogen compound or of a vinyl halogen compound alone according to the Heck reaction; a polymerization of a dialdehyde compound with a diphosphate compound according to the Horner-Wadsworth-Emmons method; a polycondensation according to the de-hydrohalogenation method of a compound having two methyl halide groups; a polycondensation according to the sulfonium salt decomposing method of a compound having two sulfonium salt groups; a polymerization of a dialdehyde compound with a diacetonitrile compound according to the Knoevenagel reaction; and a polymerization of dialdehyde compounds according to the McMurry reaction.

[0058] When a vinylene group is not contained in the main chain, there are exemplified a method in which polymerization is effected according to a Suzuki coupling reaction from the corresponding monomer, a method in which polymerization is effected according to a Grignard reaction, a method in which polymerization is effected using a Ni(0) catalyst, a method in which polymerization is effected using an oxidizing agent such as FeCl_3 and the like, a method of effecting oxidation polymerization electrochemically, a method according to decomposition of an intermediate polymer having a suitable releasing group, and the like. Of them, the method of effecting polymerization according to a Suzuki coupling reaction, the method of effecting polymerization according to a Grignard reaction, the method of effecting polymerization using a Ni(0) catalyst are preferable since reaction control is easy.

[0059] The polymeric fluorescent substance may contain a repeating unit other than repeating units represented by the formula (1) or (8), in an amount which does not deteriorate fluorescent property and charge carrying property. Further, repeating units represented by the formula (1) or (8) and other repeating units may be connected with a non-conjugation unit, or such a non-conjugation part may be contained in the repeating unit. As the bonding structure, there are exemplified those illustrated below, those obtained by combining those illustrated below with a vinylene group, those obtained by combining two or more of those illustrated below, and the like. Here, R represents a group selected from the above described groups, and Ar represents a hydrocarbon group having 6 to 60 carbon atoms.



[0060] As the divalent repeating unit, aromatic amine groups having nitrogen atom bonding are exemplified. They are atomic groups in which two hydrogen atoms are removed from an aromatic amine, and have usually about 4 to 60 carbon atoms. Here, the number of carbon atoms of the substituent is not counted as the number of carbon atoms of the divalent group. Examples thereof include specifically the following groups (represented by the following structures of Nos. 127 to 130).



[0061] The polymeric fluorescent substance may also be a random, block or graft copolymer, or a polymer having an intermediate structure thereof, for example, a random copolymer having blocking property. From the viewpoint for obtaining a polymeric fluorescent substance having high fluorescent quantum yield, random copolymers having blocking property and block or graft copolymers are more preferable than complete random copolymers. Further, copolymers may have branched main chain and three or more terminals. Dendrimers are also included.

[0062] Further, as the polymeric fluorescent substance, those emitting fluorescence in a solid state are suitably used, since the material utilizes light emission from a thin film.

[0063] As good solvents for the polymeric fluorescent substance, there are exemplified chloroform, methylene chloride, dichloroethane, tetrahydrofuran, toluene, xylene, mesitylene, tetralin, decalin, n-butylbenzene and the like. The polymeric fluorescent substance can be usually dissolved in these solvents in an amount of 0.1 wt % or more, though the amount differs depending on the structure and molecular weight of the polymeric fluorescent substance.

[0064] When these polymeric fluorescent substances are used as a light emitting material of a polymer LED, the

purity thereof exerts an influence on light emitting property, therefore, it is preferable that a monomer before polymerization is purified by a method such as distillation, sublimation purification, re-crystallization and the like before being polymerized and further, it is preferable to conduct a purification treatment such as re-precipitation purification, chromatographic separation and the like after the synthesis.

[0065] Next, the polymer LED of the present invention will be illustrated. The polymer LED of the present invention is a polymer LED comprising at least a light emitting layer between a pair of electrodes composed of an anode and a cathode at least one of which is transparent or semi-transparent wherein the light emitting layer contains a polymeric fluorescent substance of the present invention.

[0066] As the polymer LED of the present invention, there are listed polymer LEDs having an electron transporting layer disposed between a cathode and a light emitting layer, polymer LEDs having a hole transporting layer disposed between an anode and a light emitting layer, polymer LEDs having an electron transporting layer disposed between a cathode and a light emitting layer and having a hole transporting layer disposed between an anode and a light emitting layer.

[0067] For example, the following structures a) to d) are specifically exemplified.

- a) anode/light emitting layer/cathode
- b) anode/hole transporting layer/light emitting layer/cathode
- c) anode/light emitting layer/electron transporting layer/ /cathode
- d) anode/hole transporting layer/light emitting layer/electron transporting layer/cathode

(wherein, / indicates adjacent lamination of layers. Hereinafter, the same)

[0068] Herein, the light emitting layer is a layer having function to emit a light, the hole transporting layer is a layer having function to transport a hole, and the electron transporting layer is a layer having function to transport an electron. Herein, the electron transporting layer and the hole transporting layer are generically called a charge transporting layer.

[0069] The light emitting layer, hole transporting layer and electron transporting layer may also each independently used in two or more layers.

[0070] Of charge transporting layers disposed adjacent to an electrode, that having function to improve charge injecting efficiency from the electrode and having effect to decrease driving voltage of an device are particularly called sometimes a charge injecting layer (hole injecting layer, electron injecting layer) in general.

[0071] For enhancing adherence with an electrode and improving charge injection from an electrode, the above-described charge injecting layer or insulation layer having a thickness of 2 nm or less may also be provided adjacent to an electrode, and further, for enhancing adherence of the interface, preventing mixing and the like, a thin buffer layer may also be inserted into the interface of a charge transporting layer and light emitting layer.

[0072] The order and number of layers laminated and the thickness of each layer can be appropriately applied while considering light emitting efficiency and life of the device.

[0073] In the present invention, as the polymer LED having a charge injecting layer (electron injecting layer, hole injecting layer) provided, there are listed a polymer LED having a charge injecting layer provided adjacent to a cathode and a polymer LED having a charge injecting layer provided adjacent to an anode.

[0074] For example, the following structures e) to p) are specifically exemplified.

- e) anode/charge injecting layer/light emitting layer/cathode
- f) anode/light emitting layer/charge injecting layer/cathode
- g) anode/charge injecting layer/light emitting layer/charge injecting layer/cathode
- h) anode/charge, injecting layer/hole transporting layer/light emitting layer/cathode
- i) anode/hole transporting layer/light emitting layer/charge injecting layer/cathode
- j) anode/charge injecting layer/hole transporting layer/light emitting layer/charge injecting layer/cathode
- k) anode/charge injecting layer/light emitting layer/electron transporting layer/cathode
- l) anode/light emitting layer/electron transporting layer/charge injecting layer/cathode
- m) anode/charge injecting layer/light emitting layer/electron transporting layer/charge injecting layer/cathode
- n) anode/charge injecting layer/hole transporting layer/light emitting layer/electron transporting layer/cathode
- o) anode/hole transporting layer/light emitting layer/electron transporting layer/charge injecting layer/cathode
- p) anode/charge injecting layer/hole transporting layer/light emitting layer/electron transporting layer/charge injecting layer/cathode

[0075] As the specific examples of the charge injecting layer, there are exemplified layers containing an conducting polymer, layers which are disposed between an anode and a hole transporting layer and contain a material having an ionization potential between the ionization potential of an anode material and the ionization potential of a hole transporting material contained in the hole transporting layer, layers which are disposed between a cathode and an electron

transporting layer and contain a material having an electron affinity between the electron affinity of a cathode material and the electron affinity of an electron transporting material contained in the electron transporting layer, and the like.

[0076] When the above-described charge injecting layer is a layer containing an conducting polymer, the electric conductivity of the conducting polymer is preferably 10^{-5} S/cm or more and 10^3 S/cm or less, and for decreasing the leak current between light emitting pixels, more preferably 10^{-5} S/cm or more and 10^2 S/cm or less, further preferably 10^{-5} S/cm or more and 10^1 S/cm or less.

[0077] Usually, to provide an electric conductivity of the conducting polymer of 10^{-5} S/cm or more and 10^3 S/cm or less, a suitable amount of ions are doped into the conducting polymer.

[0078] Regarding the kind of an ion doped, an anion is used in a hole injecting layer and a cation is used in an electron injecting layer. As examples of the anion, a polystyrene sulfonate ion, alkylbenzene sulfonate ion, camphor sulfonate ion and the like are exemplified, and as examples of the cation, a lithium ion, sodium ion, potassium ion, tetrabutyl ammonium ion and the like are exemplified.

[0079] The thickness of the charge injecting layer is for example, from 1 nm to 100 nm, preferably from 2 nm to 50 nm.

[0080] Materials used in the charge injecting layer may properly be selected in view of relation with the materials of electrode and adjacent layers, and there are exemplified conducting polymers such as polyaniline and derivatives thereof, polythiophene and derivatives thereof, polypyrrole and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(thienylene vinylene) and derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polymers containing aromatic amine structures in the main chain or the side chain, and the like, and metal phthalocyanine (copper phthalocyanine and the like), carbon and the like.

[0081] The insulation layer having a thickness of 2 nm or less has function to make charge injection easy. As the material of the above-described insulation layer, metal fluoride, metal oxide, organic insulation materials and the like are listed. As the polymer LED having an insulation layer having a thickness of 2 nm or less, there are listed polymer LEDs having an insulation layer having a thickness of 2 nm or less provided adjacent to a cathode, and polymer LEDs having an insulation layer having a thickness of 2 nm or less provided adjacent to an anode.

[0082] Specifically, there are listed the following structures q) to ab) for example.

q) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/cathode

r) anode/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

s) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

t) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/cathode

u) anode/hole transporting layer/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

v) anode/insulation layer having a thickness of 2 nm or less/hole transporting-layer/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

w) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/electron transporting layer/cathode

x) anode/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

y) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

z) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/electron transporting layer/cathode

aa) anode/hole transporting layer/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

ab) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

[0083] In producing a polymer LED, when a film is formed from a solution by using such polymeric fluorescent substance soluble in an organic solvent, only required is removal of the solvent by drying after coating of this solution, and even in the case of mixing of a charge transporting material and a light emitting material, the same method can be applied, causing an extreme advantage in production. As the film forming method from a solution, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like.

[0084] Regarding the thickness of the light emitting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and for example, it is from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0085] In the polymer LED of the present invention, a light emitting material other than the above-mentioned polymeric fluorescent substances may be mixed in a light emitting layer. Further, in the polymer LED according to the instant application, a light emitting layer containing a light emitting material other than the above-mentioned polymeric fluo-

rescent substance may be laminated with a light emitting layer containing the above-mentioned polymeric fluorescent substance.

[0086] As the light emitting material, known materials can be used. In a compound having lower molecular weight, there can be used, for example, naphthalene derivatives, anthracene or derivatives thereof, perylene or derivatives thereof; dyes such as polymethine dyes, xanthene dyes, coumarine dyes, cyanine dyes; metal complexes of 8-hydroxyquinoline or derivatives thereof, aromatic amine, tetraphenylcyclopentane or derivatives thereof, or tetraphenylbutadiene or derivatives thereof, and the like.

[0087] Specifically, there can be used known compounds such as those described in JP-A Nos. 57-51781, 59-195393 and the like, for example.

[0088] When the polymer LED of the present invention has a hole transporting layer, as the hole transporting materials used, there are exemplified polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof, polysiloxane derivatives having an aromatic amine in the side chain or the main chain, pyrazoline derivatives, arylamine derivatives, stilbene derivatives, triphenyldiamine derivatives, polyaniline or derivatives thereof, polythiophene or derivatives thereof, polypyrrole or derivatives thereof, poly(p-phenylenevinylene) or derivatives thereof, poly(2,5-thienylenevinylene) or derivatives thereof, or the like.

[0089] Specific examples of the hole transporting material include those described in JP-A Nos. 63-70257, 63-175860, 2-135359, 2-135361, 2-209988, 3-37992 and 3-152184.

[0090] Among them, as the hole transporting materials used in the hole transporting layer, preferable are polymer hole transporting materials such as polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof, polysiloxane derivatives having an aromatic amine compound group in the side chain or the main chain, polyaniline or derivatives thereof, polythiophene or derivatives thereof, poly(p-phenylenevinylene) or derivatives thereof, poly(2,5-thienylenevinylene) or derivatives thereof, or the like, and further preferable are polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof and polysiloxane derivatives having an aromatic amine compound group in the side chain or the main chain. In the case of a hole transporting material having lower molecular weight, it is preferably dispersed in a polymer binder for use.

[0091] Polyvinylcarbazole or derivatives thereof are obtained, for example, by cation polymerization or radical polymerization from a vinyl monomer.

[0092] As the polysilane or derivatives thereof, there are exemplified compounds described in Chem. Rev., **89**, 1359 (1989) and GB 2300196 published specification, and the like. For synthesis, methods described in them can be used, and a Kipping method can be suitably used particularly.

[0093] As the polysiloxane or derivatives thereof, those having the structure of the above-described hole transporting material having lower molecular weight in the side chain or main chain, since the siloxane skeleton structure has poor hole transporting property. Particularly, there are exemplified those having an aromatic amine having hole transporting property in the side chain or main chain.

[0094] The method for forming a hole transporting layer is not restricted, and in the case of a hole transporting layer having lower molecular weight, a method in which the layer is formed from a mixed solution with a polymer binder is exemplified. In the case of a polymer hole transporting material, a method in which the layer is formed from a solution is exemplified.

[0095] The solvent used for the film forming from a solution is not particularly restricted providing it can dissolve a hole transporting material. As the solvent, there are exemplified chlorine solvents such as chloroform, methylene chloride, dichloroethane and the like, ether solvents such as tetrahydrofuran and the like, aromatic hydrocarbon solvents such as toluene, xylene and the like, ketone solvents such as acetone, methyl ethyl ketone and the like, and ester solvents such as ethyl acetate, butyl acetate, ethylcellosolve acetate and the like.

[0096] As the film forming method from a solution, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like, from a solution.

[0097] The polymer binder mixed is preferably that does not disturb charge transport extremely, and that does not have strong absorption of a visible light is suitably used. As such polymer binder, polycarbonate, polyacrylate, poly(methyl acrylate), poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polysiloxane and the like are exemplified.

[0098] Regarding the thickness of the hole transporting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and at least a thickness at which no pin hole is produced is necessary, and too large thickness is not preferable since the driving voltage of the device increases. Therefore, the thickness of the hole transporting layer is, for example, from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0099] When the polymer LED of the present invention has an electron transporting layer, known compounds are used as the electron transporting materials, and there are exemplified oxadiazole derivatives, anthraquinonedimethane or derivatives thereof, benzoquinone or derivatives thereof, naphthoquinone or derivatives thereof, anthraquinone or

derivatives thereof, tetracyanoanthraquinodimethane or derivatives thereof, fluorenone derivatives, diphenyldicyanoethylene or derivatives thereof, diphenylquinone derivatives, or metal complexes of 8-hydroxyquinoline or derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polyfluorene or derivatives thereof, and the like.

[0100] Specifically, there are exemplified those described in JP-A Nos. 63-70257, 63-175860, 2-135359, 2-135361, 2-209988, 3-37992 and 3-152184.

[0101] Among them, oxadiazole derivatives, benzoquinone or derivatives thereof, anthraquinone or derivatives thereof, or metal complexes of 8-hydroxyquinoline or derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polyfluorene or derivatives thereof are preferable, and 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole, benzoquinone, anthraquinone, tris(8-quinolinol)aluminum and polyquinoline are further preferable.

[0102] The method for forming the electron transporting layer is not particularly restricted, and in the case of an electron transporting material having lower molecular weight, a vapor deposition method from a powder, or a method of film-forming from a solution or melted state is exemplified, and in the case of a polymer electron transporting material, a method of film-forming from a solution or melted state is exemplified, respectively. When film-forming is conducted from a solution or melted state, a polymer binder may be used together.

[0103] The solvent used in the film-forming from a solution is not particularly restricted provided it can dissolve electron transporting materials and/or polymer binders. As the solvent, there are exemplified chlorine solvents such as chloroform, methylene chloride, dichloroethane and the like, ether solvents such as tetrahydrofuran and the like, aromatic hydrocarbon solvents such as toluene, xylene and the like, ketone solvents such as acetone, methyl ethyl ketone and the like, and ester solvents such as ethyl acetate, butyl acetate, ethyl cellosolve acetate and the like.

[0104] As the film-forming method from a solution or melted state, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like.

[0105] The polymer binder to be mixed is preferably that which does not extremely disturb a charge transport property, and that does not have strong absorption of a visible light is suitably used. As such polymer binder, poly(N-vinylcarbazole), polyaniline or derivatives thereof, polythiophene or derivatives thereof, poly(p-phenylene vinylene) or derivatives thereof, poly(2,5-thienylene vinylene) or derivatives thereof, polycarbonate, polyacrylate, poly(methyl acrylate), poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polysiloxane and the like are exemplified.

[0106] Regarding the thickness of the electron transporting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and at least a thickness at which no pin hole is produced is necessary, and too large thickness is not preferable since the driving voltage of the device increases. Therefore, the thickness of the electron transporting layer is, for example, from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0107] The substrate forming the polymer LED of the present invention may preferably be that does not change in forming an electrode and layers of organic materials, and there are exemplified glass, plastics, polymer film, silicon substrates and the like. In the case of an opaque substrate, it is preferable that the opposite electrode is transparent or semitransparent.

[0108] In the present invention, it is preferable that an anode is transparent or semitransparent, and as the material of this anode, electron conductive metal oxide films, semitransparent metal thin films and the like are used. Specifically, there are used indium oxide, zinc oxide, tin oxide, and films (NESA and the like) fabricated by using an electron conductive glass composed of indium-tin-oxide (ITO), indium-zinc-oxide and the like, which are metal oxide complexes, and gold, platinum, silver, copper and the like are used, and among them, ITO, indium-zinc-oxide, tin oxide are preferable. As the fabricating method, a vacuum vapor deposition method, sputtering method, ion plating method, plating method and the like are used. As the anode, there may also be used organic transparent conducting films such as polyaniline or derivatives thereof, polythiophene or derivatives thereof and the like.

[0109] The thickness of the anode can be appropriately selected while considering transmission of a light and electric conductivity, and for example, from 10 nm to 10 μ m, preferably from 20 nm to 1 μ m, further preferably from 50 nm to 500 nm.

[0110] Further, for easy charge injection, there may be provided on the anode a layer comprising a phthalocyanine derivative conducting polymers, carbon and the like, or a layer having an average film thickness of 2 nm or less comprising a metal oxide, metal fluoride, organic insulating material and the like.

[0111] As the material of a cathode used in the polymer LED of the present invention, that having lower work function is preferable. For example, there are used metals such as lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, aluminum, scandium, vanadium, zinc, yttrium, indium, cerium, samarium, europium, terbium, ytterbium and the like, or alloys comprising two or more of them, or alloys comprising one or more of them with one or more of gold, silver, platinum, copper, manganese, titanium, cobalt, nickel, tungsten and tin, graphite

or graphite intercalation compounds and the like. Examples of alloys include a magnesium-silver alloy, magnesium-indium alloy, magnesium-aluminum alloy, indium-silver alloy, lithium-aluminum alloy, lithium-magnesium alloy, lithium-indium alloy, calcium-aluminum alloy and the like. The cathode may be formed into a laminated structure of two or more layers.

[0112] The film thickness of a cathode can be appropriately selected in view of electric conductivity and durability, and for example, it is from 10 nm to 10 μ m, preferably from 20 nm to 1 μ m, further preferably from 50 nm to 500 nm.

[0113] As the method for fabricating a cathode, there are used a vacuum vapor deposition method, sputtering method, lamination method in which a metal thin film is adhered under heat and pressure, and the like. Further, there may also be provided, between a cathode and an organic layer, a layer comprising an conducting polymer, or a layer having an average film thickness of 2 nm or less comprising a metal oxide, metal fluoride, organic insulation material and the like, and after fabrication of the cathode, a protective layer may also be provided which protects the polymer LED. For stable use of the polymer LED for a long period of time, it is preferable to provide a protective layer and/or protective cover for protection of the device in order to prevent it from outside damage.

[0114] As the protective layer, there can be used a polymer compound, metal oxide, metal fluoride, metal borate and the like. As the protective cover, there can be used a glass plate, a plastic plate the surface of which has been subjected to lower-water-permeation treatment, and the like, and there is suitably used a method in which the cover is pasted with an device substrate by a thermosetting resin or light-curing resin for sealing. If space is maintained using a spacer, it is easy to prevent an device from being injured. If an inner gas such as nitrogen and argon is sealed in this space, it is possible to prevent oxidation of a cathode, and further, by placing a desiccant such as barium oxide and the like in the above-described space, it is easy to suppress the damage of an device by moisture adhered in the production process. Among them, any one means or more are preferably adopted.

[0115] For obtaining light emission in plane form using the polymer LED of the present invention, an anode and a cathode in the plane form may properly be placed so that they are laminated each other. Further, for obtaining light emission in pattern form, there are a method in which a mask with a window in pattern form is placed on the above-described plane light emitting device, a method in which an organic layer in non-light emission part is formed to obtain extremely large thickness providing substantial non-light emission, and a method in which any one of an anode or a cathode, or both of them are formed in the pattern. By forming a pattern by any of these methods and by placing some electrodes so that independent on/off is possible, there is obtained a display device of segment type which can display digits, letters, simple marks and the like. Further, for forming a dot matrix device, it may be advantageous that anodes and cathodes are made in the form of stripes and placed so that they cross at right angles. By a method in which a plurality of kinds of polymeric fluorescent substances emitting different colors of lights are placed separately or a method in which a color filter or luminescence converting filter is used, area color displays and multi color displays are obtained. A dot matrix display can be driven by passive driving, or by active driving combined with TFT and the like. These display devices can be used as a display of a computer, television, portable terminal, portable telephone, car navigation, view finder of a video camera, and the like.

[0116] Further, the above-described light emitting device in plane form is a thin self-light-emitting one, and can be suitably used as a flat light source for back-light of a liquid crystal display, or as a flat light source for illumination. Further, if a flexible plate is used, it can also be used as a curved light source or a display.

EXAMPLES

[0117] The following examples further illustrate the present invention in detail but do not limit the scope thereof.

[0118] Herein, regarding the number average molecular weight, a polystyrene reduced number-average molecular weight was measured by gel permeation chromatography (GPC) using chloroform as a solvent.

Example 1

<Synthesis of 2,6-dibromo-1,5-dihexyloxynaphthalene>

[0119] Under an inert atmosphere, sodium ethoxide (2.76g, 40.6mmol) and 2,6-dibromo-1,5-di hydroxynaphthalene (5g, 15.7mmol) were dissolved in ethanol (60ml). Under reflux, ethanol solution(10ml) of hexylbromide (6.7g, 40.6mmol) was added dropwise in 10 minutes. It was refluxed for 5 hours and then left for cooling. The reaction mixture was added to 1N sodium-hydroxide aqueous solution, and the depositing precipitate was filtrated. The precipitate was washed with methylene chloride, and the washed solution was concentrated under a reduced pressure to obtain a crude product. The desired product was obtained after purifying by silica gel chromatography (toluene:hexane =4:1).

[0120] The amount was 3.72g, and the yield was 48%.

<Synthesis of 9,9-dioctylfluorene-2,7-bis(ethylene boronate)>

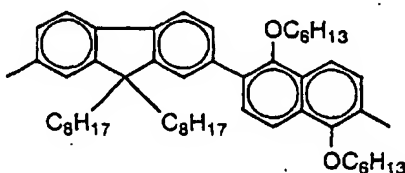
[0121] 2, 7-di bromo fluorene (25g, 77mmol), octylbromide (44.7g, 0.596 mols), sodium hydroxide (37.5g, 0.937 mols), and tetrabutyl ammonium bromide (0.5g, 1.55mmol) were dissolved in dimethyl sulfoxide (75ml)-water (37.5ml) mixed solvent. It was kept warm at 80°C for 6 hours. After cooling, toluene (100ml) and water (100ml) were added, and the organic layer was partitioned. The organic layer is washed with water, 3% hydrochloric acid, and water, and then dehydrated with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the crude product was purified by silica-gel chromatography, and 2,7-dibromo-9,9-dioctylfluorene was obtained. (Amount:26.85g, yield:79%)

[0122] The resultant 2,7-dibromo-9,9-dioctylfluorene (24.7g, 22.8mmol) was dissolved in tetrahydrofuran under an inert atmosphere, and cooled to -70°C or less. To this, 1.6M of n-butyllithium (61.9ml) was added dropwise in 40 minutes. After 2 hours stirring, trimethoxyborane (14.0g, 135mmol) was added dropwise in 5 minutes. After raising the temperature to a room temperature, the mixture was added into 5% sulfuric acid, and the organic layer was partitioned. The aqueous layer was extracted with ethylacetate, and the organic layers was collected and washed with water. The organic layer was dried by molecular sieves and the solvent was distilled off under reduced pressure. The residue was suspended in hexane, filtrated off the insoluble material, and a crude product of 9,9-dioctylfluorene-2,7-di-boronic acid was obtained (12.56g, 26.3mmol).

[0123] The crude product was dissolved in 630ml of toluene together with ethylene glycol (33.85g, 0.545 mols). 500ml of the toluene was distilled off at 115 °C, and the same amount of toluene was added. The distillation-addition was conducted repeatedly two times, left for cooling, and then the organic layer was washed with water, and dehydrated with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the crude product was purified by silica-gel chromatography (toluene:ethylacetate=5:1), and 9,9-dioctylfluorene-2,7-bis(ethylene boronate). The amount was 6.65g, and the yield was 54%.

<Synthesis of poly(9,9-dioctylfluorene-1,5-dihexyloxy-2,6-naphthalene)>

[0124] Under an inert atmosphere, 9,9-dioctylfluorene-2,7-bis(ethylene boronate) (305 mg, 0.574 mmol), 2,6-dibromo-1,5-dihexyloxynaphthalene (266 mg, 0.549 mmol) and aliquat® 336 (tricaprylmethylammonium chloride, manufactured by Aldrich, 200 mg, 0.497 mmol) were dissolved in toluene (10 ml) and to this was added 10 ml of an aqueous solution of potassium carbonate (225 mg, 1.49 mmol). Further, tetrakis(triphenylphosphine)palladium (19 mg, 0.015 mmol) was added, and the mixture was heated under reflux for 20 hours. After cooling, the solution was separated, and the organic layer was washed with water. This organic layer was dropped into methanol, and the deposited precipitate was filtrated off to obtain Polymeric fluorescent substance 1'. The yield was 190 mg. By NMR, it was confirmed that the obtained polymer has a following repeating unit expected from the charged monomer.



[0125] Polymeric fluorescent substance 1' had a polystyrene-reduced number-average molecular weight of 1.9×10^4 . Polymeric fluorescent substance 1 could be dissolved in a solvent such as toluene, chloroform and the like.

<Evaluation of fluorescent property>

[0126] A 0.4 wt% chloroform solution of Polymeric fluorescent substance 1 was spin-coated on quartz, to form a thin film of Polymeric fluorescent substance 1'. The ultraviolet visible absorption spectrum and fluorescent spectrum of this thin film were measured by using a ultraviolet visible absorption spectrophotometer (UV3500 manufactured by Hitachi, Ltd.) and a fluorescent spectrophotometer (850 manufactured by Hitachi, Ltd.), respectively. For calculation of fluorescent strength, a fluorescent spectrum excited at 350 nm was used. The area of fluorescent spectra plotted against wave-number on the abscissa was divided by the absorption at 350 nm, to obtain a relative value of the fluorescent strength.

[0127] Polymeric fluorescent substance 1' has a fluorescent peak wave-length of 484 nm, and revealed a relative value of the fluorescent strength of 2.0.

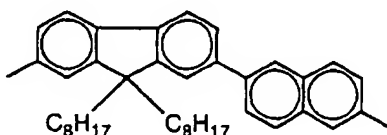
<Production and evaluation of the device>

[0128] On a glass substrate on which an ITO film had been made at a thickness of 150 nm according to a sputtering method, a film having a thickness of 50 nm was formed using a solution (Baytron, manufactured by Bayer) of poly (ethylenedioxythiophene)/polystyrenesulfonic acid by spin coating, and the film was dried at 120°C for 10 minutes on a hot plate. Then, a film having a thickness of about 70 nm was formed using a 1.5 wt% toluene solution of Polymeric fluorescent substance 1' by spin coating. Further, this film was dried at 80°C for 1 hour under reduced pressure, then, lithium fluoride was vapor-deposited at 0.4 nm as a cathode buffer layer, calcium was vapor-deposited at 25 nm and aluminum was vapor-deposited at 40 nm as a cathode, to produce a polymer LED. In any vapor deposition, the degree of vacuum was 1 to 8×10^{-6} Torr. Voltage was applied on the resulted device, to give EL light emission from Polymeric fluorescent substance 1'. The strength of EL light emission was approximately in proportion to the current density. Maximum light emitting efficiency was about 1.4 cd/A.

Comparative Example 1

<Synthesis of poly(9,9-dioctylfluorene-1,5-naphthalene)>

[0129] Under an inert atmosphere, 9,9-dioctylfluorene-2,7-bis(ethylene boronate) (305 mg, 0.574 mmol), 2,6-dibromonaphthalene (142 mg, 0.549 mmol) and aliquat® 336 (tricaprylylmethylammonium chloride, manufactured by Aldrich, 200 mg, 0.497 mmol) were dissolved in toluene (10 ml) and to this was added 10 ml of an aqueous solution of potassium carbonate (225 mg, 1.49 mmol). Further, tetrakis(triphenylphosphine) palladium (19 mg, 0.015 mmol) was added, and the mixture was heated under reflux for 20 hours. After cooling, the solution was separated, and the organic layer was washed with water. This organic layer was dropped into methanol, and the deposited precipitate was filtrated off to obtain Polymeric fluorescent substance 2'. The yield was 99 mg. By NMR, it was confirmed that the obtained polymer has a following repeating unit expected from the charged monomer.



[0130] Polymeric fluorescent substance 2' had a polystyrene-reduced number-average molecular weight of 2.0×10^4 . Polymeric fluorescent substance 2' could be dissolved in a solvent such as toluene, chloroform and the like.

<Evaluation of fluorescent property>

[0131] The relative value of the fluorescent strength of polymeric fluorescent substance 2' was obtained as the same manner with Example 1.

[0132] Polymeric fluorescent substance 2' has a fluorescent peak wave-length of 428 nm, and a relative value of the fluorescent strength of 0.42.

<Production and evaluation of the device>

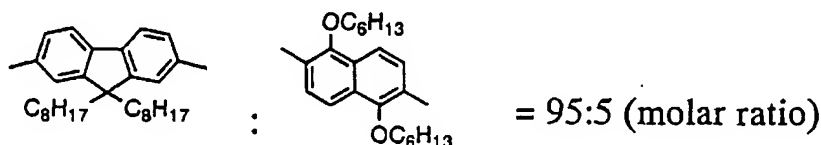
[0133] A polymer LED was produced as the same manner with Example 1 except that polymeric fluorescent substance 2' was used instead of polymeric fluorescent substance 1'. Voltage was applied on the resulted device, to give EL light emission from Polymeric fluorescent substance 2'. The strength of EL light emission was approximately in proportion to the current density. Maximum light emitting efficiency was about 0.1 cd/A.

Example 2

<Synthesis of poly(9,9-dioctylfluorene-co-1,5-dihexyloxy-2,6-naphthalene)>

[0134] Under an inert atmosphere, 9,9-dioctylfluorene-2,7-bis(ethylene boronate) (305 mg, 0.574 mmol), 2,7-dibromo-9,9-dioctylfluorene (270 mg, 0.492 mmol), 2,6-dibromo-1,5-dihexyloxynaphthalene (26.6 mg, 0.0549 mmol), and aliquat® 336 (tricaprylylmethylammonium chloride, manufactured by Aldrich, 200 mg, 0.549 mmol) were dissolved

in toluene (10 ml) and to this was added 10 ml of an aqueous solution of potassium carbonate (238 mg, 1.72 mmol). Further, tetrakis(triphenylphosphine)palladium (1.27 mg, 0.0011 mmol) was added, and the mixture was heated under reflux for 10 hours. After cooling, the solution was separated, and the organic layer was washed with water. This organic layer was dropped into methanol, and the deposited precipitate was filtrated off to obtain Polymeric fluorescent substance 3'. The yield was 280 mg. By NMR, it was confirmed that the obtained polymer has a following repeating unit expected from the charged monomer.



[0135] Polymeric fluorescent substance 3' had a polystyrene-reduced number-average molecular weight of 3.5×10^4 . Polymeric fluorescent substance 3' could be dissolved in a solvent such as toluene, and chloroform.

<Evaluation of fluorescent property>

[0136] The relative value of the fluorescent strength of polymeric fluorescent substance 3' was obtained as the same manner with Example 1.

[0137] Polymeric fluorescent substance 3' has a fluorescent peak wave-length of 426 nm, and a relative value of the fluorescent strength of 4.98.

Referential Example 1

<Synthesis of naphthalene-1,4-dicarboxylic acid diethyl ester>

[0138] 40.0g of naphthalene-1,4-dicarboxylic acid, and 50g of concentrated sulfuric acid were added to 415 ml of ethanol. After heating for 6 hours with reflux, ethanol was distilled off. Extraction from the residue was carried out with toluene/water. The organic layer was washed with 3% aqueous solution of sodium bicarbonate, dried by sodium sulfate, concentrated with using an evaporator, and isolated by column chromatography (silica-gel/toluene:ethyl acetate). 37.8g of naphthalene-1,4-dicarboxylic-acid diethyl ester was obtained as the desired product.

Referential Example 2

<Synthesis of 6-bromonaphthalene-1,4-dicarboxylic-acid diethyl ester>

[0139] Naphthalene-1,4-dicarboxylic-acid diethyl ester 35.0g was dissolved in a mixed solvents 280ml of methylene chloride and concentrated sulfuric acid (weight ratio 3:7), and N-bromo succinimide 22.9g was added here at a room temperature. After stirring overnight, the reaction mixture was poured into ice, and extracted with ethyl acetate. The extracted solution was washed with diluted alkaline water, subsequently with water, and then dried by magnesium sulfate. The solution was concentrated, and treaded with column processing (silica gel/chloroform), and 28.0g of a crude product of 6-bromonaphthalene-1,4-dicarboxylic-acid diethyl ester was obtained.

Referential Example 3

<Synthesis of 6'-(4-(3,7-dimethyloctyloxy)phenyl) naphthalene 1,4-dicarboxylic-acid diethyl ester>

[0140] Under argon atmosphere and in a toluene/water mixed solvent, 6-bromonaphthalene-1,4-dicarboxylic-acid diethyl ester 4.5g and 4-(3,7-dimethyloctyloxy)phenyl boric acid 4.0g were reacted with using tetrakis(triphenylphosphine)palladium under a condition of usual Suzuki reaction. Purification by column treatment (silica gel/toluene) was carried out, and 6-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene-1,4-dicarboxylic-acid diethyl ester 3.5g was obtained.

Referential Example 4

<Synthesis of 1,4-bis(hydroxymethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene>

[0141] Under argon atmosphere and with cooling in ice, 10.0ml of THF solutions of LiAlH_4 (1.0M) was added to 6-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene-1,4-dicarboxylic acid diethyl ester 1.42g in THF solution, and stirred at a temperature as it was, for 3 hours.

[0142] Purification by column treatment (silica gel/toluene:ethyl acetate) was carried out, and 1.48g crude product of 1,4-bis(hydroxymethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl) naphthalene was obtained.

Referential Example 5

<Synthesis of 1,4-bis(chloromethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene>

[0143] Under nitrogen atmosphere, 1.40g of a crude product of 1,4-bis(hydroxymethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene was dispersed in chloroform, and 1.29g of thionyl chloride was added dropwise at a room temperature, to result a complete solution system quickly.

[0144] Purification by column treatment (silica gel/toluene-hexane) was carried out, and 1,4-bis(chloromethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl) naphthalene 1.07g was obtained.

$^1\text{H-NMR}$ (200MHz / CDCl_3)
 δ 0.88ppm (d, 6H)

0.96 ppm (d, 3H)

1.18-1.89 ppm (m, 10H)

4.06 ppm (t, 2H)

5.02 ppm (s, 2H)

5.05 Ppm (s, 2H)

7.04 ppm (d, 2H)

7.42 ppm (d, 1H)

7.47 ppm (D, 1H)

7.67 ppm (d, 2H)

7.86 ppm (dd, 1H)

8.21 ppm (d, 1H)

8.30 ppm (dd, 1H)

Referential Example 6

<Synthesis of 1,4-bis(bromomethyl)-2-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene>

[0145] 1,4-dimethyl-2-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene was prepared in accordance with the case of 6-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene-1,4-dicarboxylic acid diethyl ester described above, but using 1,4-dimethyl-2-bromonaphthalene, as a raw material, which was obtained by brominating 1,4-dimethylnaphthalene with Br_2 . 1,4-dimethyl-2-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene was dissolved in carbon tetrachloride, and reacted to NBS to obtain 1,4-bis(bromomethyl)-2-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene was obtained.

Referential Example 7

<Synthesis of 2,6-bis(chloromethyl)-4-(4-(3,7-dimethyloctyloxy)phenyl)naphthalene>

[0146] This compound was prepared in accordance with the case of 1,4-bis(chloromethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl) naphthalene described above, with using naphthalene-2,6-dicarboxylic acid-as a raw material.

Example 3

<Synthesis of polymeric fluorescent substance 4>

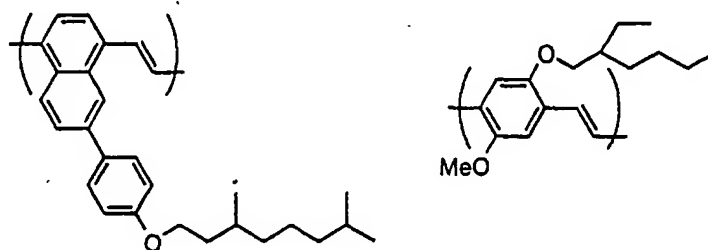
[0147] 1,4-bis(chloromethyl)-6-(4-(3,7-dimethyloctyloxy)phenyl) naphthalene 0.23g and 2-methoxy-5-(2-ethylhexyloxy)-p-xylylene dichloride 0.167g were dissolved in 1,4-dioxane (dehydration) 135ml, then by nitrogen gas bubbling,

the atmosphere in the system was replaced with nitrogen gas. This solution was raised to 95°C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.52g in 1,4-dioxane (dehydration) 15ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently, it was reacted at 95°C for 2.5 hours in nitrogen-gas atmosphere.

[0148] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.17g of a polymer was obtained.

[0149] Next, after dissolving the polymer in chloroform, reprecipitation purification was conducted by a method of methanol addition to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.16g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 4.

[0150] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 4 was 3.3×10^4 .



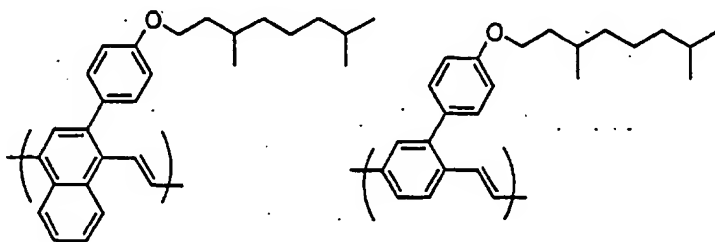
Example 4

<Synthesis of polymeric fluorescent substance 5>

[0151] 1,4-bis(bromomethyl)-2-{4-(3,7-dimethyloctyloxy)phenyl} naphthalene 0.546g was reacted with triethyl phosphite, and a phosphonic ester was produced. The resulting phosphonic ester 0.66g and 1,4-diformyl-2-{4'-(3,7-dimethyloctyloxy) phenyl}benzene 0.366g were dissolved in THF(dehydration)35ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.67g in THF (dehydration) 20ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 20 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0152] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and 0.57g of a polymer was obtained. Next, after dissolving the polymer in about 30ml of THF, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at reduced pressure and 0.42g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 5.

[0153] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 5 was 1.4×10^4 .



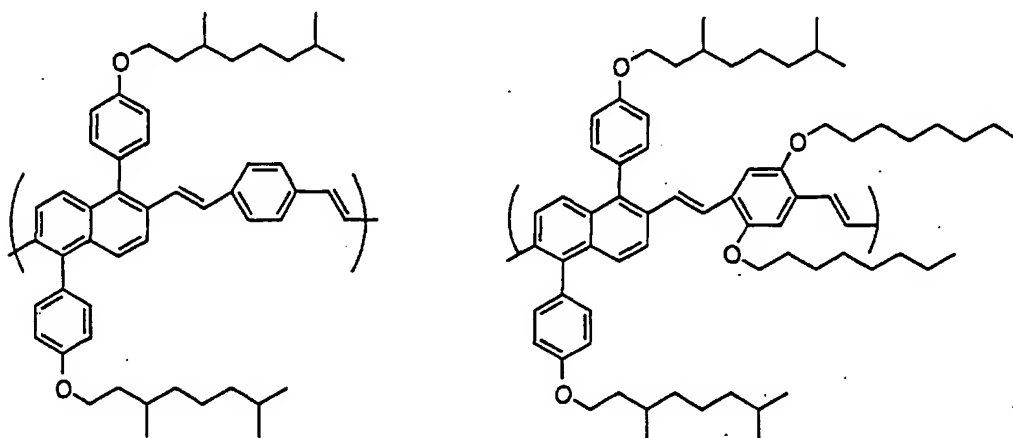
Example 5

<Synthesis of polymeric fluorescent substance 6>

[0154] 2,6-bis(bromomethyl)-1,5-bis[4'-(3,7-dimethyloctyloxy)phenyl] naphthalene 0.778g was reacted with triethylphosphite, and a phosphonic ester was produced. The resulting phosphonic ester 0.892g, terephthalaldehyde 0.113g and 2,5-dioctyloxyterephthalaldehyde 0.0624g were dissolved in THF(dehydration)35ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.67g in THF (dehydration) 30ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0155] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and 0.65g of a polymer was obtained. Next, after dissolving the polymer in about 30g of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.45g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 6.

[0156] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 6 was 1.2×10^4 .



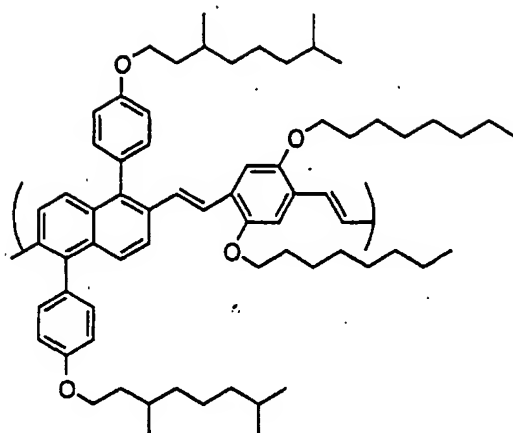
Example 6

<Synthesis of polymeric fluorescent substance 7>

[0157] 2,6-bis(bromomethyl)-1,5-bis[4'-(3,7-dimethyloctyloxy) phenyl]naphthalene 0.610g was reacted with triethylphosphite, and a phosphonic ester was produced. The resulting phosphonic ester 0.700g, and 2,5-dioctyloxyterephthalaldehyde 0.306g were dissolved in THF(dehydration)40ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.46g in THF (dehydration) 15ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0158] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and some amount of a polymer was obtained. Next, after dissolving the polymer in about 23ml of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.69g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 7.

[0159] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 7 was 1.9×10^4 .



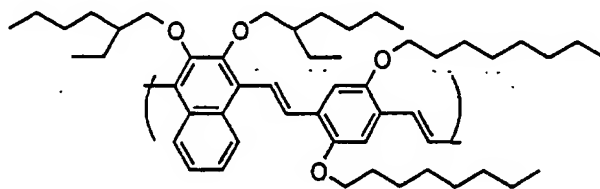
Example 7

<Synthesis of polymeric fluorescent substance 8>

[0160] 1,4-bis(bromomethyl)-2,3-bis(2-ethylhexyloxy)naphthalene 4.360g was reacted with triethylphosphite, and a phosphonic ester 5.04g was produced. The resulting phosphonic ester 0.734g and 2,5-dioctyloxyterephthalaldehyde 0.43g were dissolved in THF(dehydration)40ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.46g in THF (dehydration) 15ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0161] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and some amount of a polymer was obtained. Next, after dissolving the polymer in about 23ml of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.16g of a polymer was obtained. The resulting polymer is referred to as Polymeric-fluorescent substance 8.

[0162] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 8 was 4.9×10^3 .



Example 8

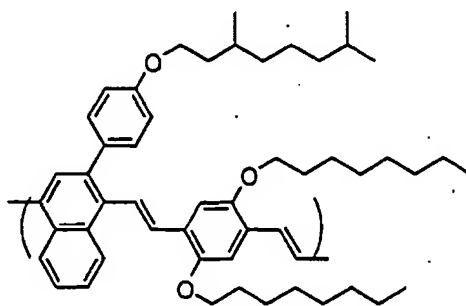
<Synthesis of polymeric fluorescent substance 9>

[0163] 1,4-bis(bromomethyl)-3-{4'-(3,7-dimethyloctyloxy)phenyl} naphthalene 1.530g was reacted with triethylphosphite, and a phosphonic ester 1.73g was produced. The resulting phosphonic ester 0.713g and 2,5-dioctyloxyterephthalaldehyde 0.43g were dissolved in THF(dehydration)40ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.46g in THF (dehydration) 15ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0164] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting

precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and some amount of a polymer was obtained. Next, after dissolving the polymer in about 23ml of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.10g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 9.

[0165] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 9 was 7.8×10^3 .



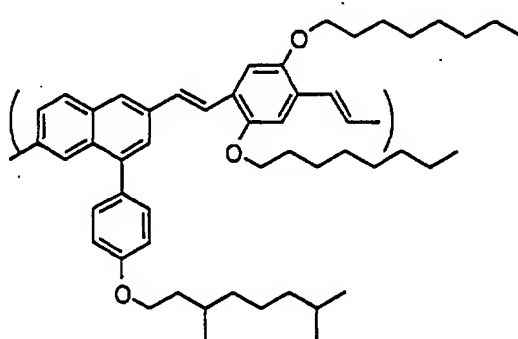
Example 9

<Synthesis of polymeric fluorescent substance 10>

[0166] 2,6-bis(bromomethyl)-4-(4'-(3,7-dimethyloctyloxy)phenyl) naphthalene 0.710g was reacted with triethylphosphite, and a phosphonic ester was produced. The resulting phosphonic ester 0.330g and 2,5-dioctyloxyterephthalaldehyde 0.195g were dissolved in THF(dehydration)18g, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert'-butoxide 0.23g in THF (dehydration) 7ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0167] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and some amount of a polymer was obtained. Next, after dissolving the polymer in about 23ml of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.21g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 10.

[0168] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 10 was 7.1×10^3 .



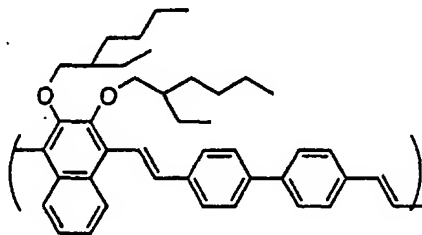
Example 10

<Synthesis of polymeric fluorescent substance 11>

[0169] 1,4-bis(bromomethyl)-2,3-bis(2-ethylhexyloxy)naphthalene 4.360g was reacted with triethylphosphite, and a phosphonic ester 5.04g was produced. The resulting phosphonic ester 0.680g and 4,4'-diformylbiphenyl 0.21g were dissolved in THF(dehydration)40ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.336g in THF (dehydration) 15ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0170] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and a polymer was obtained. Next, after dissolving the polymer in about 23ml of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.10g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 11.

[0171] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 11 was 1.5×10^3 .



Example 11

<Synthesis of polymeric fluorescent substance 12>

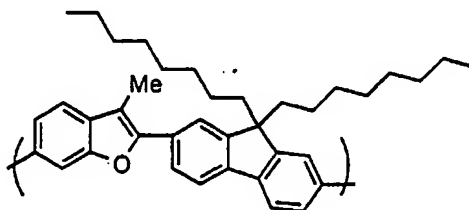
[0172] 1,4-bis(bromomethyl)-2,3-bis(2-ethylhexyloxy)naphthalene 4.360g was reacted with triethyl phosphite, and a phosphonic ester 5.04g was produced. The resulting phosphonic ester 0.340g and 9,9-bis(3,7-dimethyloctyl)-2,7-diformyl-fluorene 0.251g were dissolved in THF(dehydration)20ml, then, the atmosphere in the system was replaced with nitrogen gas by nitrogen gas bubbling. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.20g in THF (dehydration) 7ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added at a room temperature in about 10 minutes. Subsequently, it was reacted at room temperature for 4 hours in nitrogen-gas atmosphere.

[0173] After the reaction, this solution was neutralized with adding acetic acid and poured into methanol, and resulting precipitate was collected. Next, this precipitate was washed with ethanol, dried under reduced pressure and some amount of a polymer was obtained. Next, after dissolving the polymer in about 23ml of chloroform, methanol was added therein and resulting precipitate was collected. The precipitate was washed by ethanol, then dried at a reduced pressure and 0.10g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 12.

[0174] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 12 was 7.0×10^3 .

of 1 mol/L was charged. The mixture solution was refluxed for 15 hours to react. After the reaction, the solution was cooled and dropped into methanol:water (10:1/W:W) solution. The deposited solid was taken out and loosened in 70ml of methanol. The resulting powdery solid was filtrated and dissolved in 15ml of toluene, which was dropped into methanol 70ml to deposit a solid. The solid was filtrated and powdery solid was obtained. The precipitate was dried at a reduced pressure and 0.101g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 14.

[0179] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 14 was 7.5×10^3 .

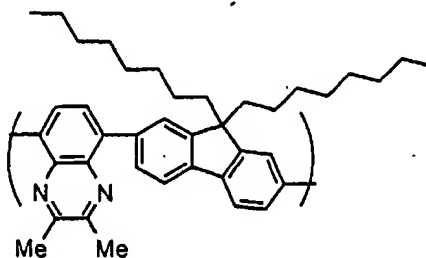


Example 14

<Synthesis of polymeric fluorescent substance 15>

[0180] 9,9-di-n-octylfluorene-2,7-di(ethylene boronate) 0.240g and 5,8-dibromo-2,3-dimethylquinoxaline 0.136g were dissolved in toluene 6ml, and the atmosphere of the system was replaced with argon gas. Next, aliquat® 336 (manufactured by Aldrich) 22mg and tetrakis triphenylphosphine palladium complex 3mg were charged into this solution. Furthermore, 1.46g of potassium carbonate aqueous solution having a concentration of 1 mol/L was charged. The mixture solution was refluxed for 10 hours to react. After the reaction, the solution was cooled and dropped into methanol:water (10:1/W:W) solution. The deposited solid was taken out and loosened in 67ml of methanol. The resulting powdery solid was filtrated and dissolved in 14ml of toluene, which was dropped into methanol 67ml to deposit a solid. The solid was filtrated and powdery solid was obtained. The precipitate was dried at a reduced pressure and 0.213g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 15.

[0181] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 15 was 1.55×10^4 .



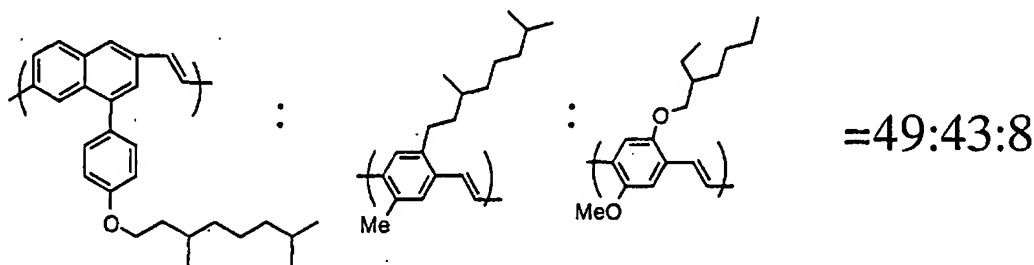
Example 15

<Synthesis of polymeric fluorescent substance 16>

[0182] 2,6-bis(chloromethyl)-4-{4'-(3,7-dimethyloctyloxy)phenyl} naphthalene 0.457g, 2-methoxy-5-(2-ethylhexyloxy)-p-xylylene dichloride 0.0533g and 2-methyl-5-(3,7-dimethyloctyl)-p-xylylene dibromide 0.360g were dissolved in 1,4-dioxane (dehydration) 270ml, then by nitrogen gas bubbling, the atmosphere of the system was replaced with nitrogen gas. This solution was raised to 95°C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 1.1g in 1,4-dioxane (dehydration) 30ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently, it was reacted at 95°C for 2.5 hours in nitrogen-gas atmosphere.

[0183] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.33g of a polymer was obtained. Next, after dissolving the polymer in THF, reprecipitation purification was conducted by adding methanol to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.25g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 16.

[0184] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 16 was 5.4×10^4 .



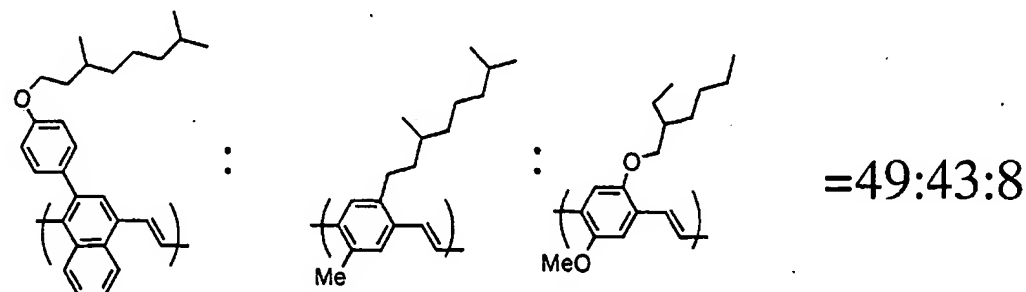
Example 16

<Synthesis of polymeric fluorescent substance 17>

[0185] 1,4-bis(bromomethyl)-2-{4'-(3,7-dimethyloctyloxyphenyl) naphthalene 0.457g, 2-methoxy-5-(2-ethylhexyloxy)-p-xylylene dichloride 0.0533g and 2-methyl-5-(3,7-dimethyloctyl)-p-xylylene dibromide 0.360g were dissolved in 1,4-dioxane (dehydration) 270ml, then by nitrogen gas bubbling, the atmosphere of the system was replaced with nitrogen gas. This solution was raised to 95°C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 1.1g in 1,4-dioxane (dehydration) 30ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently, it was reacted at 95°C for 3 hours in nitrogen-gas atmosphere.

[0186] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.30g of a polymer was obtained. Next, after dissolving the polymer in THF, reprecipitation purification was conducted by adding methanol to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.21g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 17.

[0187] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 17 was 4.5×10^4 .



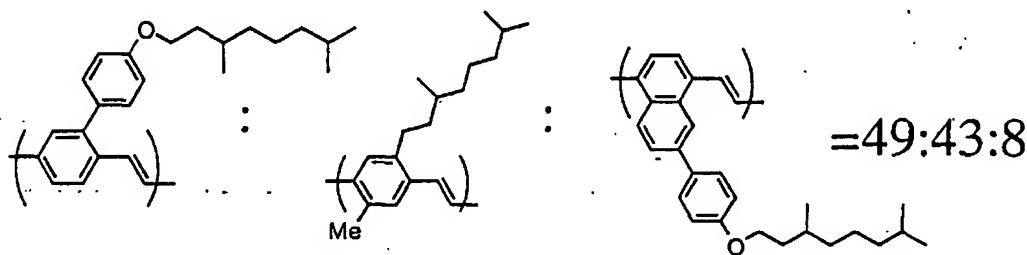
Example 17

<Synthesis of polymeric fluorescent substance 18>

[0188] 1,4-bis(bromomethyl)-6-[4'-(3,7-dimethyloctyloxyphenyl) naphthalene 0.0732g, 2-[4'-(3,7-dimethyloctyloxyphenyl)-p-xylylene dichloride 0.407g and 2-methyl-5-(3,7-dimethyloctyl)-p-xylylene dibromide 0.360g were dissolved in 1,4-dioxane (dehydration) 270ml, then by nitrogen gas bubbling, the atmosphere of the system was replaced with nitrogen gas. This solution was raised to 95°C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 1.1g in 1,4-dioxane (dehydration) 30ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently, it was reacted at 95° C for 2.5 hours in nitrogen-gas atmosphere.

[0189] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.36g of a polymer was obtained. Next, after dissolving the polymer in THF, reprecipitation purification was conducted by adding methanol to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.36g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 18.

[0190] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 18 was 1.6×10^5 .



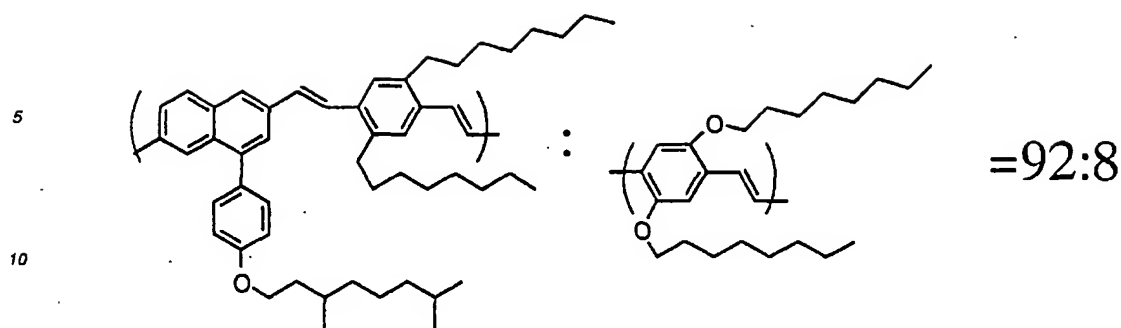
Example 18

<Synthesis of polymeric fluorescent substance 19>

[0191] 2,6-diformyl-4-[4'-(3,7-dimethyloctyloxy)phenyl]naphthalene 0.208g, 2,5-di-n-octyloxy-p-xylylene diphosphonic acid diethyl ester 0.301g, 2,5-di-n-octyloxy-1,4-terephthalaldehyde 0.0156g and 2,5-di-n-octyloxy-p-xylylene diphosphonic acid diethyl ester 0.0254g were dissolved in THF (dehydration) 20ml, then by nitrogen gas bubbling, the atmosphere of the system was replaced with nitrogen gas. This solution was raised to 95°C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.336g in THF (dehydration) 5ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently, it was reacted at 95°C for 2.5 hours in nitrogen-gas atmosphere.

[0192] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.29g of a polymer was obtained. Next, after dissolving the polymer in THF, reprecipitation purification was conducted by adding methanol to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.15g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 19.

[0193] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 19 was 7.3×10^3 .



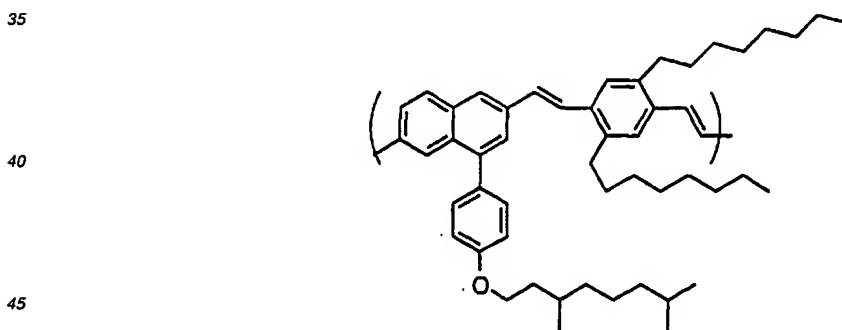
15 Example 19

<Synthesis of polymeric fluorescent substance 20>

20 [0194] 2,6-diformyl-4-{4'-(3,7-dimethyloctyloxy)phenyl}naphth alene 0.208g and 2,5-di-n-octyl-p-xylylene diphosphonic acid diethyl ester 0.301g were dissolved in THF (dehydration) 20ml, then by nitrogen gas bubbling, the atmosphere of the system was replaced with nitrogen gas. This solution was raised to 95°C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.336g in THF (dehydration) 5ml and replacing the-atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently,

25 [0195] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.29g of a polymer was obtained. Next, after dissolving the polymer in THF, reprecipitation purification was conducted by adding methanol to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.25g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 20.

30 [0196] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 20 was 4.4×10^3 .



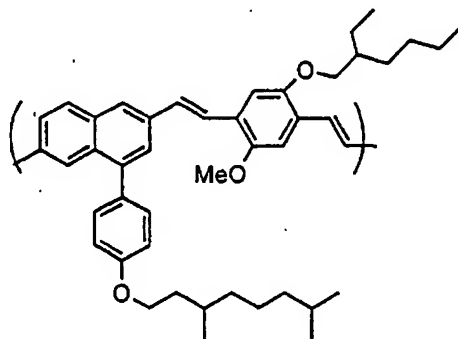
50 Example 20

<Synthesis of polymeric fluorescent substance 21>

55 [0197] 2,6-diformyl-4-{4'-(3,7-dimethyloctyloxy)phenyl}naphth alene 0.208g and 2-methoxy-5-(2-ethylhexyloxy)-p-xylylene diphosphonic acid diethyl ester 0.268g were dissolved in THF (dehydration) 20ml, then by nitrogen gas bubbling, the atmosphere of the system was replaced with nitrogen gas. This solution was raised to 95° C in nitrogen-gas atmosphere. Then, to this solution, a solution obtained by dissolving potassium tert-butoxide 0.336g in THF (dehydration) 5ml and replacing the atmosphere with nitrogen gas by nitrogen gas bubbling, was added in about 10 minutes. Subsequently, it was reacted at 95° C for 2.5 hours in nitrogen-gas atmosphere.

[0198] After cooling, this solution was neutralized with adding acetic acid. About 200ml of methanol was added to the solution and resulting precipitate was collected. Next, this precipitate was washed with ethanol and dried under reduced pressure, then 0.29g of a polymer was obtained. Next, after dissolving the polymer in THF, reprecipitation purification was conducted by adding methanol to this solution. The resulting precipitate was washed by ethanol, then dried at reduced pressure and 0.28g of a polymer was obtained. The resulting polymer is referred to as Polymeric fluorescent substance 21.

[0199] The polystyrene reduced number average molecular weight of polymeric fluorescent substance 21 was 5.5×10^3 .



Example 21

<Evaluation of fluorescent property>

[0200] A 0.4 wt% chloroform solution of each of polymeric fluorescent substances 4 to 21 were spin-coated on quartz, to form a thin film of polymeric fluorescent substance 4 to 21, respectively. The ultraviolet visible absorption spectrum and fluorescent spectrum of the thin films were measured by using a ultraviolet visible absorption spectrophotometer (UV3500 manufactured by Hitachi, Ltd.) and a fluorescent spectrophotometer (850 manufactured by Hitachi, Ltd.), respectively. For calculation of fluorescent strength, a fluorescent spectrum excited at 410 nm was used. The area of fluorescent spectra plotted against wave-number on the abscissa was divided by the absorption at 410 nm, to obtain a relative value of the fluorescent strength.

[0201] The fluorescent peak wave-lengths and relative values of the fluorescent strength of the polymeric fluorescent substances 1 to 18 are shown in Table 1.

Table 1

Fluorescent properties of polymeric fluorescent substances		
Polymeric fluorescent substance	Fluorescent peak wave-length (nm)	Fluorescent strength (a.u.)
4	618	0.09
5	544	1.11
6	524	2.11
7	540	1.09
8	558	0.63
9	572	0.44
10	568	0.12
11	496	2.00
12	504	1.66
13	480	1.05
14	446	0.82

Table 1 (continued)

Fluorescent properties of polymeric fluorescent substances		
Polymeric fluorescent substance	Fluorescent peak wave-length (nm)	Fluorescent strength (a.u.)
15	480	0.33
16	554	1.66
17	552	0.59
18	574	0.29
19	554	1.37
20	538	1.68
21	566	0.36

Example 22

<Production and evaluation of the device>

[0202] On a glass substrate on which an ITO film had been made at a thickness of 150 nm according to a sputtering method, a film having a thickness of 50 nm was formed using a solution (Baytron, manufactured by Bayer) of poly (ethylenedioxythiophene)/polystyrenesulfonic acid by spin coating, and the film was dried at 120°C for 10 minutes on a hot plate. Then, a film having a thickness of about 60 nm was formed using a 0.75 wt% toluene solution of polymeric fluorescent substance 16 by spin coating. Further, this film was dried at 80°C for 1 hour under reduced pressure, then, with using aluminum alloy containing 0.5 wt% of lithium, aluminum-lithium alloy was vapor-deposited at about 40 nm as a cathode to produce a polymer LED. In any vapor deposition, the degree of vacuum was 1 to 8×10^{-6} Torr. Voltage was applied on the resulted device, to give EL light emission from the polymeric fluorescent substance. The strength of EL light emission was approximately in proportion to the current density. Voltage at which the luminance exceeds 1 cd/m² was 2.3V and the maximum light emitting efficiency was 3.5 cd/A.

Example 23

[0203] A polymer LED was produced as the same manner with the above Example except that a 0.95 wt% chloroform solution of polymeric fluorescent substance 20. Voltage was applied on the resulted device, to give EL light emission from the polymeric fluorescent substance. The strength of EL light emission was approximately in proportion to the current density. Voltage at which the luminance exceeds 1 cd/m² was 3.0V and the maximum light emitting efficiency was 4.0 cd/A.

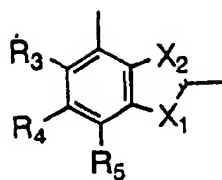
[0204] The polymeric fluorescent substance of the present invention contains a condensed aromatic ring such as naphthalene and an arylene group such as fluorene, and shows strong fluorescence, and can be suitably used as a polymer LED or a pigment for laser. The polymer LED using this polymeric fluorescent substance is a polymer LED of high performance which can be driven at lower voltage with high efficiency. Therefore, this polymer LED can be preferably used as a back light of a liquid crystal display, a light source in the form of curved surface or flat surface for illumination, or a display device of segment type, and in apparatuses such as a flat panel display of dot matrix, and the like.

Claims

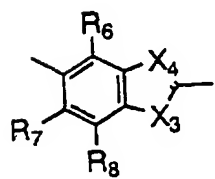
1. A polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 1×10^3 to 1×10^8 , and comprising one or more repeating units of formula (1):



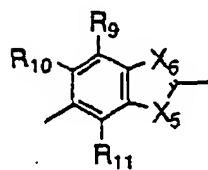
wherein Ar₁ is a divalent group represented by the following formulae (2) to (7):



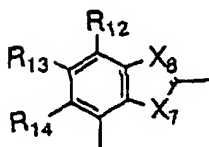
(2)



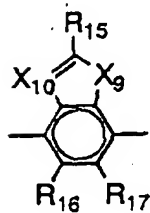
(3)



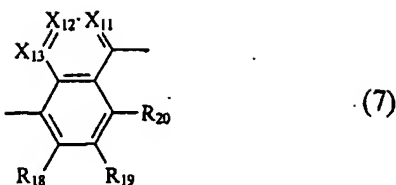
(4)



(5)



(6)



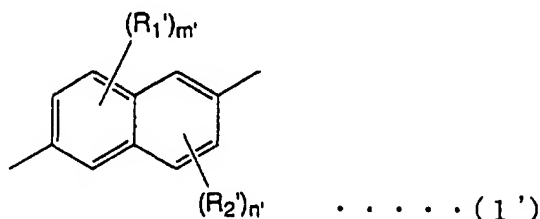
10 wherein X_1 , X_3 , X_5 , X_7 and X_9 each independently represent a group selected from $-\text{CR}_{21}=\text{CR}_{22}-$, $-\text{CR}_{23}=\text{N}-$, $-\text{N}=\text{CR}_{24}-$, $-\text{O}-\text{CO}-$, $-\text{CR}_{25}\text{R}_{26}-$, $-\text{CO}-$, $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{NR}_{27}-$ and $-\text{SiR}_{28}\text{R}_{29}-$; X_2 , X_4 , X_6 , X_8 , X_{10} , X_{11} , X_{12} and X_{13} each independently represent a group selected from $-\text{CR}_{30}=$ and $-\text{N}=$; R_3 to R_{30} each independently represent a hydrogen atom or a substituent selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group and cyano group; and at least one of R_3 to R_{30} is not a hydrogen atom; R_1 and R_2 each independently represent a group selected from a hydrogen atom, alkyl groups, aryl groups, monovalent heterocyclic compound groups and cyano group; and n is 0 or 1; and

20 one or more repeating units of formula (8):



25 wherein Ar_2 represents an arylene group or divalent heterocyclic compound group, but the group is not represented by any of formulae (2) to (7); Ar_2 may have one or more substituents; when Ar_2 has a plurality of substituents, they may be the same or different; R_{36} and R_{37} each independently represent a group selected from a hydrogen atom, alkyl groups, aryl groups, monovalent heterocyclic compound groups and a cyano group; and m represents 0 or 1.

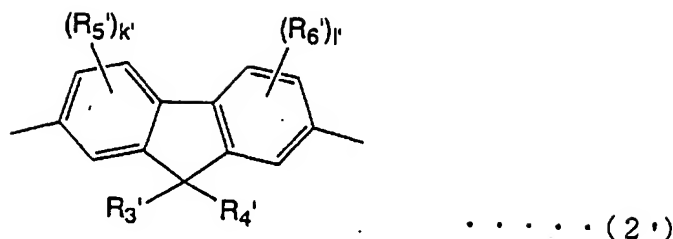
- 30 2. A substance according to claim 1 wherein Ar_1 has one or more substituents selected from an aryl group and a monovalent heterocyclic compound group.
3. A substance according to claim 1 or 2 wherein Ar_1 is represented by formula (1'):



45 wherein R_1' and R_2' each independently represent a group selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; m' and n' are each independently integers of 0-3 provided that m' and n' are not 0 simultaneously; when m' is two or more, two or more R_1' may be the same or different; when n' is two or more, a plurality of R_2' may be the same or different; and R_1' and R_2' may be connected to form a ring.

50

4. A substance according to any one of claims 1 to 3 wherein Ar_2 is represented by formula (2'):
- 55



wherein R_3' and R_4' each independently represent a group selected from a hydrogen atom, alkyl group, aryl group, and a heterocyclic compound group; R_5' and R_6' each independently represent a group selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; k' and l' are each independently integers of 0-3; when k' is two or more, a plurality of R_5' may be the same or different; when l' is two or more, a plurality of R_6' may be the same or different; and R_3' to R_6' may be connected to form a ring.

5. A substance according to any one of claims 1 to 4 wherein the total amount of repeating units of formulae (1) and (8) is 50 mol% or more based on the total amount of all repeating units, and the amount of repeating units of formula (1) is 0.1 mol% or more and 95 mol% or less based on the total amount of the repeating units of formulae (1) and (8).
6. A substance according to any one of claims 1 to 5 wherein the total amount of repeating units of formulae (1) and (8) is 50 mol% or more based on the total amount of all repeating units, and the amount of repeating units of formula (1) is 5 mol% or more and 95 mol% or less based on the total amount of the repeating units of formulae (1) and (8).
7. A polymer light emitting device comprising at least a light emitting layer between a pair of electrodes composed of an anode and a cathode at least one of which is transparent or semi-transparent wherein the light emitting layer comprises a polymeric fluorescent substance according to any one of claims 1 to 6.
8. A device according to claim 7, further comprising a layer comprising a conducting polymer disposed between one electrode and the light emitting layer such that the layer comprising a conducting polymer is adjacent to said electrode.
9. A device according to claim 7 or 8, further comprising an insulation layer having a thickness of 2 nm or less disposed between one electrode and the light emitting layer such that the insulation layer is adjacent to said electrode.
10. A device according to any one of claims 7 to 9, further comprising a layer comprising an electron transporting compound disposed between the cathode and the light emitting layer such that the layer comprising an electron transporting compound is adjacent to said light emitting layer.
11. A device according to any one of claims 7 to 10, further comprising a layer comprising a hole transporting compound disposed between the anode and the light emitting layer such that the layer comprising a hole transporting compound is adjacent to said light emitting layer.
12. A device according to any one of claims 7 to 11, further comprising a layer comprising an electron transporting compound and a layer comprising a hole transporting compound disposed between the cathode and the light emitting layer such that the layer comprising an electron transporting compound is adjacent to said light emitting layer, and the layer comprising a hole transporting compound is adjacent to said light emitting layer.
13. A flat light source comprising a polymer light emitting device according to any one of claims 7 to 12.
14. A segment display comprising a polymer light emitting device according to any one of claims 7 to 12.
15. A dot matrix display comprising a polymer light emitting device according to any one of claims 7 to 12.

16. A liquid crystal display comprising a polymer light emitting device according to any one of claims 7 to 12 as a back-light.

5

10

15

20

25

30

35

40

45

50

55



(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
04.09.2002 Bulletin 2002/36

(51) Int Cl.7: **C09K 11/06**

(43) Date of publication A2:
12.06.2002 Bulletin 2002/24

(21) Application number: **01310199.3**

(22) Date of filing: **05.12.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

- Tsubata, Yoshiaki
Tsukuba-shi, Ibaraki (JP)
- Ueoka, Takahiro
Tsukuba-shi, Ibaraki (JP)
- Sasaki, Shigeru
Tsukuba-shi, Ibaraki (JP)
- Noguchi, Takanobu
Tsukuba-shi, Ibaraki (JP)

(30) Priority: **06.12.2000 JP 2000371180**
30.03.2001 JP 2001100626

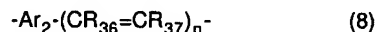
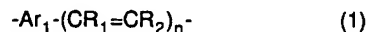
(71) Applicant: **Sumitomo Chemical Company,**
Limited
Chuo-ku Osaka 541-8550 (JP)

(74) Representative: **Cresswell, Thomas Anthony**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5JJ (GB)

(72) Inventors:
• **Doi, Shuji**
Tsukuba-shi, Ibaraki (JP)

(54) **Polymeric fluorescent substance and polymer light-emitting device using the same**

(57) A polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 1×10^3 to 1×10^8 , and comprising one, or more repeating units of formula (1) and one or more repeating units of formula (8):



wherein Ar_1 represents a specific arylene or a divalent heterocyclic compound group, and Ar_2 represent an arylene or a divalent heterocyclic compound group other than Ar_1 . By using the polymeric fluorescent substance, a high performance polymer LED can easily be obtained.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 31 0199

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X,P	US 6 299 796 B1 (IGARASHI TATSUYA) 9 October 2001 (2001-10-09) * column 2, line 26-46; claim 4 * * column 6, line 10-15 * * column 3, line 36-46,51-55 * ----	1,2	C09K11/06
X	EP 0 725 120 A (SUMITOMO CHEMICAL CO) 7 August 1996 (1996-08-07) * page 4, line 10-35; claim 1 * ----	3	
X	* page 5, line 23-25 * * page 8, line 15-30,55-58; claim 1 * ----	4	
A	WO 99 20675 A (DOW CHEMICAL CO) 29 April 1999 (1999-04-29) * page 6 - page 7; claims 1-11 * ----	1-16	
A	US 5 298 189 A (KAUFFMAN JOEL M) 29 March 1994 (1994-03-29) * column 15 - column 18; claims 1-16 * ----	1-16	
A	US 5 792 568 A (EMOTO KAZUHIRO ET AL) 11 August 1998 (1998-08-11) * column 3, line 10 - column 4; claims 1-26 * ----	1-16	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C09K H05B
A	EP 0 763 532 A (DAINIPPON PRINTING CO LTD) 19 March 1997 (1997-03-19) * page 3 - page 6; claims 1,2,5,12-17 * ----	1,5-16	
A	US 5 518 656 A (FURUTA YASUSI ET AL) 21 May 1996 (1996-05-21) * column 3, line 65 - column 4, line 48; claims 1-7 * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 June 2002	Examiner Wengeler, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document			

EPC FORM 1503 03/82 (PO/C01)



European Patent
Office

Application Number
EP 01 31 0199

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



European Patent
Office

LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 01 31 0199

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1,5-16

CLAIMS 1, 5-16: A polymeric fluorescent substance comprising one or more repeating units of formula (1)-Ar1-(CR1=CR2)n- and formula(8)-Ar2-(CR36=CR37)n-.

A polymer light emitting device, a flat light source, a segment display, a dot matrix display and a liquid crystal display comprising polymers of formula (1) and (8).

2. Claim : 2

CLAIM 2: Substance according to claim 1 in which -Ar1- has substituents selected from aryl and monovalent heterocyclic compound groups

3. Claim : 3

CLAIM 3: Substance according to claim 1 in which -Ar1- is represented by formula (1')

4. Claim : 4

CLAIM 4: Substance according to claim 1 in which -Ar2- is represented by formula (2').

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 31 0199

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-06-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 6299796	B1	09-10-2001	JP	11185959 A	09-07-1999
EP 0725120	A	07-08-1996	DE	69600529 D1	24-09-1998
			DE	69600529 T2	25-02-1999
			EP	0725120 A1	07-08-1996
			JP	9045478 A	14-02-1997
			US	5821002 A	13-10-1998
WO 9920675	A	29-04-1999	US	5777070 A	07-07-1998
			CA	2305137 A1	29-04-1999
			CN	1276806 T	13-12-2000
			EP	1025142 A1	09-08-2000
			JP	2001520289 T	30-10-2001
			TW	412544 B	21-11-2000
			WO	9920675 A1	29-04-1999
US 5298189	A	29-03-1994	NONE		
US 5792568	A	11-08-1998	JP	8298183 A	12-11-1996
			JP	8306490 A	22-11-1996
EP 0763532	A	19-03-1997	JP	9059266 A	04-03-1997
			JP	9059267 A	04-03-1997
			JP	9255670 A	30-09-1997
			EP	0763532 A2	19-03-1997
			US	5980779 A	09-11-1999
			US	5766510 A	16-06-1998
			JP	9316442 A	09-12-1997
US 5518656	A	21-05-1996	NONE		

EPO FORM P0456

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82